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PROCEEDINGS

OF

THE ROYAL SOCIETY.

"On the Combining Properties of Serum-Complements and on Complementoids."

By ROBERT MUIR, M.D., Professor of Pathology, University of Glasgow, and CARL H. BROWNING, M.B., Ch.B., Joseph Coats Research Scholar, University of Glasgow.

Communicated by Sir J. S. BURDON-SANDERSON, Bart., F.R.S. Received May 17,—Read June 9, 1904.

The combining properties of serum-complement have been studied in two chief relationships. In the first place, its combination with red corpuscles or bacteria, through the medium of the appropriate immune-body, has been investigated to a certain extent, and facts of considerable importance have been obtained. Taking the case of hæmolytic sera, we may for the present put aside the question whether the immune-body acts as a link (amboceptor) between the molecule of the red corpuscle and complement (Ehrlich's view), or whether complement enters into direct combination with the molecules of the red corpuscles through the influence of the immune-body. If we represent the combining molecules or receptors of the red corpuscles by R, and the immune-body by IB, it is sufficient for our present purpose to recognise that C combines with R + IB. In the second place, complement enters into combination with the anti-complement developed in the serum of an animal of different species by injection of complement into that animal; we may thus speak of the combination of C with anti-C. It may be recalled that Ehrlich regards complement as consisting of two chief atom groups, viz., a haptophore or combining group, and a zymotoxic, by which it produces its characteristic effect. He also concludes, as the result of an ingenious series of experiments* in conjunction with Morgenroth, that the anti-complement fills up the haptophore group of complement, and thus prevents combination with red corpuscles united to immune-body, *i.e.*, with R + IB molecules.

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* Ehrlich and Morgenroth, Berlin, 'Klin. Woch.,' 1900, No. 31.

A particular anti-complement has, as a rule, the greatest neutralising effect on the complement used for its production, though it may have an action also on the complements of some other animals, whilst on others still it has little or no effect. This would point to a difference in the haptophore groups of the several complements. Yet these may be effective in hæmolysis, *i.e.*, they may combine with the R + IB molecules, and therefore the haptophore groups of these different complements would appear to be the same. This apparent contradiction has been discussed by Bordet* and by Ehrlich and Morgenroth,† and the latter observers suggest that there may be more than one immune-body, one combining with the complement of animal A and another combining that of animal B. It seemed to us that this and other questions might be investigated by the method devised by one of us,‡ by means of which the amount of complement taken up by the R + IB molecules can be estimated. We can thus determine whether these molecules saturated for the complement of one species are also saturated for that of another species. The present paper falls into two chief parts, the first dealing with the combining affinities of complement for anti-complement and for R + IB molecules respectively, the second dealing with complementoids.

The methods used of estimating the value of immune-body and of complement are those of Ehrlich and V. Dungern, as explained in a previous paper. We shall use the following abbreviations:—C = complement, anti-C = anti-complement, IB = immune body, R = the receptors of the red corpuscles which combine with immune-body, M.H.D. = minimum hæmolytic dose. When we are speaking of doses, a numeral is placed before the symbol, thus, 3IB will mean three times the amount of immune-body necessary for hæmolysis in presence of excess of complement, and 3R + 3IB will signify three doses of IB, combined with the corresponding number of receptors of the red corpuscles; R + IB + C will, of course, indicate a condition leading to complete hæmolysis.

I.—*On the Combining (Haptophore) Group of Complement.*

(a) *On the Firmness of the Combinations of Complement.*—In the first place we may consider the relative stability of the combination $C + \overline{R + IB}$ on the one hand and the combination C + anti-C on the other hand. It has been shown by one of us in a previous communication that in the particular instance studied§ there is no evidence that C after combination with R + IB can be dissociated, but it will be well to give a detailed experiment in illustration. The red corpuscles of the ox saturated with the corresponding IB obtained from the rabbit can take up about 8—9 hæmolytic doses of guinea-pig's C, and if we make the suspension of red corpuscles four times the usual strength, *i.e.*, 20 per cent., then 1 c.c. of such a suspension will take up more than 30 doses of C. We can then test whether any of the C is recoverable. The following are the details:—

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* Bordet, 'Annales de l'Inst. Pasteur,' 1901, p. 303.

† Ehrlich and Morgenroth, *op. cit.*

‡ Muir, 'The Lancet,' 1903, vol. 2, p. 446.

§ It must be noted that the results obtained apply only to the particular conditions investigated, and must be interpreted in that light.

1. 1 c.c. of a 20-per-cent. suspension of ox's corpuscles in salt solution is placed in a test-tube, and there are added (*a*) more than sufficient IB to saturate the corpuscles, (*b*) 1 c.c. of guinea-pig's C (the M.H.D. is 0·055 c.c.), so that nearly twenty doses are added.

2. The tube is placed in the incubator for 2 hours at 37° C., the contents being well shaken from time to time.

3. At the end of 2 hours 0·5 c.c. of a 5-per-cent. suspension of ox corpuscles, treated with IB, is added (the hæmolytic dose of C for this is, of course, 0·027 c.c.); the tube is placed in the incubator for another hour.

4. The contents of the tube are then centrifugalised, and the corpuscles are washed with salt solution to remove the red fluid. The corpuscles are then laked with water, and compared with 0·5 c.c. suspension of red corpuscles similarly treated.

The result is that no perceptible hæmolysis of the added corpuscles has taken place. By the method employed the hæmolysis of less than a fifth of the corpuscles is readily detected, *i.e.*, if 0·005 c.c. of C were recoverable, this would be shown by the resulting hæmolysis. Such an experiment, therefore, shows (*a*) that practically complete combination of the added complement takes place, and (*b*) that of the combined complement not 1 per cent. can be dissociated.

When the saturation point has been reached, *i.e.*, when C is first obtainable, any C then added remains free to a large extent. In a former paper it was stated that, as a rule, a single dose of C added remains free, but further experiments show that this is rather the exception. It sometimes occurs, but usually after the saturation point more than one dose of C requires to be added to give one dose free. Considerable variations occur in this respect, and we are unable to explain them, though possibly the presence of a certain proportion of complementoid mixed with the complement may be the cause. This, however, does not affect the statement regarding the firmness of the union of C with R + IB after combination has taken place.

When we come to the combination of C with anti-C, we find that quite another condition obtains. Here we have an exaggerated instance of what Ehrlich found in the case of a toxin and anti-toxin, *viz.*, that when a neutral mixture of those substances is made, and time is allowed for combination, the addition of several lethal doses of toxin may be necessary before a lethal dose remains free. The following may be taken as examples:—

1. C of guinea-pig; M.H.D. = 0·03 c.c.

Anti-C to guinea-pig's C obtained by injecting a rabbit with guinea-pig's serum.

To each of a series of tubes containing 0·5 c.c. salt solution 0·1 c.c. anti-C is added, and to the several tubes 0·03, 0·04, 0·5 c.c., etc., of guinea-pig's C is added. The tubes are placed in the incubator at 37° C. for an hour.

The amount of C obtainable in each tube is tested by adding to each 1 c.c. suspension of red corpuscles, treated with IB, and incubating for an hour, the tubes being afterwards placed in a cool chamber for 16 hours.

It is found that in the tube containing 0·03 c.c. C a mere trace of lysis has occurred, in the tube 0·04 c.c. C half the corpuscles have undergone solution, but it is not till the tube containing 0·12 c.c. C is reached that complete hæmolysis of the corpuscles has occurred. In other words, if we take the tube where C is first obtainable from the mixture of C and anti-C, three additional doses of C must be added before a full hæmolytic dose is obtainable.

2. In this case 0·05 c.c. anti-C is used, and the M.H.D. of C is 0·05 c.c. The procedure is the same as before. The result is that even from the tube containing 0·03 c.c. of C a trace of C is obtainable, but a full hæmolytic dose is got first in the tube containing 0·1 c.c. of C, *i.e.*, one-and-a-half hæmolytic doses must be added ere one remains free. (It is to be noted that here the amount of anti-C is only half of what it was in the previous case.)

Such results, which agree with those of Bordet, clearly show that with a mixture of C and anti-C there is no sharp line of neutralisation. On the contrary, even with *relatively* small amounts of C and anti-C, if we determine the point at which C is first obtainable, then several doses of C must be added before a full dose is obtainable. We have avoided using the term "free C" with reference to the C which is obtainable from such mixtures, because we believe that part of the C is got by dissociation. Of this there is distinct evidence. In every case where red corpuscles treated with IB are added to a mixture of C and anti-C, and complete lysis has not occurred, it is found that after the corpuscles have been allowed to settle, a zone of diffusion of hæmoglobin is seen above the sedimented corpuscles. This is evidently to be explained on the supposition that in such a tube there is, in addition to the combined C, a minute trace of free C. This latter combines with the red corpuscles, and according to the law regarding substances loosely combined, a small quantity of C is dissociated from the combination C + anti-C to take its place. This process is repeated during the sedimentation of the red corpuscles, and the result is an additional amount of solution of hæmoglobin. Such a phenomenon is not seen in ordinary test-tube experiments, where there is incomplete lysis with a mixture merely of C and IB. It follows from what we have said that we consider it to be impossible to determine by such methods the exact point at which C remains free in a mixture of C and anti-C; we can only determine how much C is obtainable, and this amount will be in excess of the free C, because part of it is got by dissociation.

As is well known, Ehrlich explained the analogous phenomenon in the case of diphtheria toxin and anti-toxin by supposing that in the "toxin" there is a mixture of toxin in the proper sense and degenerated toxin or toxoid, the latter having little toxic action and also, as a rule, a feebler combining affinity. Bordet,* on the other hand, explains the phenomenon in the case of complement and anti-complement by the hypothesis that an anti-complement molecule has no fixed combining relationship, but may become united to one, two, three, etc., complement molecules, so that we have AC^1, AC^2, AC^3 combinations. Madsen, Dreyer, and Arrhenius,† from a number of very important researches on tetanolysin and diphtheria toxin, come to the conclusion that the union of toxin and anti-toxin follows the chemical law of Guldberg and Waage for substances whose combining affinity is somewhat feeble. In other words, the combination belongs to the category of reversible actions, the amount of the two substances in combination having always a definite relationship to the amount of each of the two substances free. We have not worked out with sufficient fullness the behaviour of C and anti-C to make a definite statement on this point; we may, however, state that the results which we have got present a close analogy to those of the Danish observers. It should be noted, however, that the nature of the union of toxin or complement with its anti-substance is one matter, the question as to the existence of toxoids and complementoids is another.

(*b*) *On the Specific Affinities of the Haptophore Group.*—There is another way in which the combinations of C with anti-C and R + IB molecules respectively may be compared, namely, as regards specific affinities.

1. Using the anti-C to guinea-pig's C obtained from the rabbit, we find in confirmation of Ehrlich and Morgenroth that this anti-C has some effect on rabbit's C, though it is very slight. In a given case, for example, we found that the addition of 0·1 c.c. anti-C to the M.H.D. of rabbit's C scarcely diminishes the amount of lysis which follows when the test amount of red corpuscles treated with IB is added; there is merely a slight deposit in the tube as compared with the control, and 0·6 of a M.H.D. of C has to be added before this disappears, *i.e.*, 1·6 M.H.D. treated with 0·1 c.c. anti-C produces quite complete hæmolysis. With guinea-pig's complement 0·1 c.c. anti-C with a little more than the M.H.D. of C prevents lysis almost completely, and three additional doses of C must be added to the mixture before complete lysis occurs when the test is made in the same way

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* Bordet, 'Annales de l'Inst. Pasteur,' vol. 17, 1903, p. 161.

† *Vide* 'Festskrift ved Indvielsen af Statens Serum Institut,' Copenhagen, 1902; also Madsen, 'Centralbl. f. Bakteriol.,' vol. 34, p. 630.

(*vide supra*), *i.e.*, 4M.H.D. treated with 0·1 c.c. anti-C produces lysis. The anti-C has thus a marked effect on guinea-pig's C as compared with that on rabbit's C. One would conclude that while some of the molecules in the rabbit's C and in the guinea-pig's C have the same combining affinity, most of the molecules in the rabbit's C do not combine with the anti-C, *i.e.*, have a different haptophore group from that of the molecules of guinea-pig's complement.

2. How do the complements behave towards the same R+IB molecules? As is well known, ox's corpuscles, treated with IB from the rabbit, are lysed on the addition either of guinea-pig's C or of rabbit's C. This would point to the haptophore groups of the two complements being the same. Ehrlich and Morgenroth have supposed in the corresponding case of the IB to rabbit's corpuscles obtained from the guinea-pig, that there are really two IB's present, one of which combines with the rabbit's complement and one with the guinea-pig's, and point out in favour of this view that when rabbit's C is used, the M.H.D. of IB is about ten times greater than when guinea-pig's C is used. We have accordingly investigated the case of the immune-body obtained by injecting the rabbit with ox's corpuscles. As both rabbit's and guinea-pig's complements are taken up by ox's corpuscles combined with immune-body, the question comes to be whether both complements combine with the same molecules. Does the combination of guinea-pig's complement prevent the combination of rabbit's complement and *vice versâ*? We have conducted a large number of experiments of this nature, and the result has always been to give an answer in the affirmative. The experiments are on the same lines as those already described. Suppose we wish to test how much guinea-pig's complement is kept from combination by the previous combination of a given amount of rabbit's complement. To one series (A) of tubes, each containing the test amount of corpuscles combined with the same amount of IB (generally 3—4 D), we add increasing amounts of guinea-pig's complement and test how much the treated corpuscles will take up. In another series (B) of similar tubes, we add a given amount of rabbit's C, allow combination to take place for an hour at 37° C., and then test as before how much guinea-pig's C will be taken up. (It is convenient in such experiments to produce lysis first of all in all the tubes, in a case such as the present by guinea-pig's C. The amount of C used, of course, is added to the final result.) The excess in the amount of guinea-pig's C taken up in series A over that taken up in series B gives the amount which has been kept out by the amount of rabbit's C used. The following may be cited as examples:—

1. No. 3. M.H.D. of guinea-pig's C = 0·05 c.c.; M.H.D. of rabbit's C = 0·22 c.c. About 3D of IB added to each of two series of tubes, each tube containing 1 c.c. suspension of red corpuscles.

Series A. Guinea-pig's C alone added. Amount taken up = 0·24 c.c.

Series B. 0·25 c.c. rabbit's C first, and then guinea-pig's C. Amount of guinea-pig's C taken up = 0·19 c.c.

Therefore, 0·25 c.c. of rabbit's C has kept from combination about 0·05 c.c. guinea-pig's C.

2. No. 24. M.H.D. of guinea-pig's C = 0·04 c.c.; M.H.D. of rabbit's C = 0·3 c.c. About 3D of IB added to each tube as before.

Series A. Rabbit's C alone added; amount taken up = 1·35 c.c.

Series B. 0·04 c.c. of guinea-pig's C first, and then rabbit's C. Amount of rabbit's C taken up = 0·9 c.c.

Therefore, 0·04 c.c. of guinea-pig's C has kept out 0·45 rabbit's C.

3. No. 31. M.H.D. of guinea-pig's C = 0·0175 c.c.; M.H.D. of rabbit's C = 0·1 c.c., 4D of IB added to each tube.

Series A. Guinea-pig's C alone added. Amount taken up = 0·11 c.c.

Series B. 0·1 c.c. of rabbit's C first, and then guinea-pig's C. Amount of guinea-pig's C taken up = 0·09 c.c.

Therefore, 0·1 c.c. rabbit's C has kept out 0·02 c.c. guinea-pig's C.

Another method is to determine whether R + IB molecules saturated, say, for rabbit's complement are also saturated for guinea-pig's complement. To one series (A) of tubes, each containing the same amount of red corpuscles and the same amount of IB, complement of rabbit is added in increasing amounts, and the tubes are placed in the incubator for 2 hours at 37° C. The same procedure is carried out in another series (B), but at the end of the 2 hours a hæmolytic dose of guinea-pig's C is added to each tube. The tubes of both series are placed in the incubator for another hour, and the presence of free C is tested for in the usual way. It is evident that the first series will give the point of saturation with rabbit's C, and the corresponding tube in the second series will show whether such a tube can still take up guinea-pig's complement. As an example, in one experiment it is found that in series A the tube with 0·2 c.c. rabbit's C added gives a fifth of a hæmolytic dose of free C, whilst in series B the tube containing 0·2 c.c. rabbit's C gives a full hæmolytic dose of free C. Thus it is shown that the tube saturated with rabbit's C took up not more than a fifth of a dose of guinea-pig's C. (A separate estimation carried out at the same time gave 0·14 c.c. as the amount of guinea-pig's C taken up by the same amount of red corpuscles treated with IB.) It will be shown below that a corresponding result is obtained by saturation with complementoids.

We have, therefore, shown that in the case studied practically all the molecules of the guinea-pig's complement combine with the same R + IB molecules of the ox as the molecules of the rabbit's complement combine with.

Another interesting point which presents itself is whether the hæmolytic value of a complement corresponds with the combining value. The hæmolytic dose of normal rabbit's serum in the case studied is always several times that of guinea-pig's complement. This may be because there are fewer complement molecules in a given amount of rabbit's serum or because the zymotoxic group of the rabbit's complement is less active than that of the guinea-pig's complement. In the former case a hæmolytic dose of rabbit's complement will prevent the combination of a hæmolytic dose of guinea-pig's complement; in the latter it will prevent the combination of more. Our experiments are not sufficiently extensive to give a definite statement on this point, especially in view of the fact that during the progress of an experiment the hæmolytic action of complement may diminish, and this change in the value does not always occur in the two complements in the same proportion. We may say, however, that we have obtained in several instances a correspondence between the combining and the hæmolytic ratio, *i.e.*, a hæmolytic dose of guinea-pig's complement keeps out a dose of rabbit's, and *vice versâ*. We are inclined to think that this may be the rule in the case before us, and that probably the divergences in these ratios which we have also met with are the result of accidental disturbing causes. We do not consider this point as satisfactorily settled. It is to be noted that the M.H.D. of the IB is practically the same, with the two complements used, provided that the natural IB of the guinea-pig's serum for the ox's corpuscles be first removed. In other cases recently investigated by us where this does not hold, a distinct difference between combining relationships and hæmolytic action has been brought out.

Conclusion.

It is seen (1) that the firmness of combination is much greater in the case of C with R + IB molecules than of C with anti-C, and (2) that differences in the combining affinities of the C's of two animals brought out when tested with anti-C may not obtain when tested with R + IB. The latter result involves an apparent contradiction, but is probably to be explained by the energy of combination in the two cases. It is quite intelligible that differences shown to exist where the chemical union is of a loose nature may not be detectable when the combining affinity is strong. The relation of a toxin or complement to its corresponding anti-substance is often compared to that of a key to a lock, but the above results show that this is not accurate, as the comparison would involve that two different keys can be forced into the same lock. Complements which may be shown by their behaviour to anti-complements to be different, may still act as if they were similar in the processes of hæmolysis and, probably, of bacteriolysis.

II.—*On Complementoids and their Combination.*

Ehrlich has pointed out the analogy which exists between complements and toxins of various kinds. Looked at from the point of view of the red corpuscle or bacterium, the complement is the toxic agent which leads to its partial or complete destruction, the auxiliary action of the immune-body being, however, necessary. From his study of changes which occur in toxins and their neutralisation by anti-toxin, he came to the conclusion that the toxophore group might undergo degeneration while the haptophore group survived, though its combining energy might be weakened. To such an altered toxin he gave the name toxoid. The results of hæmolytic studies led him to the conclusion that a similar change might occur in complements, the result being complementoids. The chief evidence for the existence of complementoids is the following:—

In most cases when normal sera are heated to 55° C. for an hour, the characteristic action (hæmolysis, bacteriolysis) of complement is lost, but such a serum when injected into an animal of different species has the faculty of leading to the formation of anti-complement. Hence, apparently the zymotoxic group of the complement has been destroyed, while the haptophore remains. Again, Ehrlich and Sachs* showed in the case of the hæmolytic action which the dog's serum normally possesses towards the guinea-pig's corpuscles, that the combining group of the R + IB molecules might be filled up by complementoid, and thus the action of complement, *i.e.*, hæmolysis, might be prevented. In most instances, however, this is not the case, and we must conclude either that complementoid does not usually combine with R + IB, or that if it does, it can be displaced by complement. So far as we know, the existence of complementoids in such heated sera has not been shown by test-tube experiments, though the production of anti-complements by them is strong presumptive evidence in favour of their existence. We accordingly bring forward the following methods which prove their existence:—

Is Complementoid present in Serum heated at 55° C.?

We have demonstrated the existence of complementoids by two methods, viz.: (1) by showing that they combine with R + IB molecules after lysis, and thus prevent a certain amount of C from being taken up; (2) by showing that they combine with anti-C, and thus diminish the amount of C which can be neutralised by a given amount of anti-C. We may state that the complement to be tested has usually been heated for 1½ hours at 57° C., and in every case a test was made, to show that it was devoid of hæmolytic power.

(1) As was shown by Ehrlich and Morgenroth, the addition of Cd to red corpuscles treated with IB does not prevent the combination of C and the occurrence of lysis. We may represent this as follows, the small circle indicating a red corpuscle:—

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* Ehrlich and Sachs, 'Berlin Klin. Woch.,' 1902, No. 21.

$$O\left\{\begin{matrix}R\\ IB\end{matrix}\right.+Cd\;\;\vdots\;\;+C\;\;\vdots\;\;\text{Result = lysis.}$$

The vertical dotted line indicates *a period of incubation for* 1 *hour*, unless when otherwise stated.

After lysis has occurred, however, Cd can combine with the R + IB molecules. It has been shown that a large amount of C can be taken up through the medium of multiple doses of IB, and that the combination of C is a firm one. Thus:—

$$O4\left\{\begin{matrix}R\\ IB\end{matrix}\right.+4C\;\;\overset{\text{2 hrs.}}{\vdots}\;\;+O\left\{\begin{matrix}R\\ IB\end{matrix}\right.\;\;\vdots\;\;\begin{matrix}\text{Result = no lysis in added}\\ \text{corpuscles.}\end{matrix}$$

If, however, we add in the same case 3Cd after lysis by 1C, but before the addition of the other 3C, the result is different, thus:—

$$\underset{\text{Lysis}}{O4\left\{\begin{matrix}R\\ IB\end{matrix}\right.+C}\;\;\vdots\;\;+3Cd\;\;\vdots\;\;+3C\;\;\overset{\text{2 hrs.}}{\vdots}\;\;+O\left\{\begin{matrix}R\\ IB\end{matrix}\right.\;\;\vdots\;\;\begin{matrix}\text{Result = lysis in}\\ \text{added corpuscles.}\end{matrix}$$

In other words, the Cd molecules have united with the R + IB molecules after lysis, and have prevented the added C from being taken up; this is shown by the test corpuscles undergoing lysis by means of the free C.

To avoid repetition, we may here state that the stages of all such experiments are the following:—

1. To each of a series of tubes containing the standard amount of corpuscles, a certain amount of IB is added, usually three to four hæmolytic doses.

2. To each tube is added a little more than the hæmolytic dose of complement, and a certain amount of complementoid (heated serum). The tubes are placed in the incubator for an hour at 37° C. Hæmolysis, of course, occurs, and time is allowed for the Cd to combine with the R + IB molecules.

3. To the several tubes in series complement is then added in increasing amount. Experience shows how much C is likely to be taken up, and the last tubes should, of course, contain more than this. The tubes are incubated at 37° C. for 2 hours.

4. To each tube is added the standard amount of red corpuscles, treated previously with 3D of IB, and the tubes are placed in the incubator for another hour. Hæmolysis will, of course, take place in the added corpuscles according to the amount of uncombined C present in each tube. The tubes are then placed in a cool chamber till next morning; the red fluid in each tube is pipetted off, and the amount of sedimented corpuscles left is estimated as above described.

In a control set of tubes complement only is added, and we thus ascertain how much C is taken up when no Cd is present. It is then seen how much C has been prevented from combining with the R + IB molecules by means of a given amount of Cd.

(2) Complementoid combines with anti-complement, and prevents the union of the latter with complement.

If the ordinary action of anti-complement is shown thus,

$$\text{Anti-C} + \text{C} \;\vdots\; \cdot + \bigcirc \left\{ \begin{matrix} \text{R} \\ \text{IB} \end{matrix} \right. \;\vdots\; \text{Result} = \text{no lysis},$$

then we may represent the effect of Cd by the following scheme—

$$\text{Anti-C} + \text{Cd} \;\vdots\; + \text{C} \;\vdots\; + \bigcirc \left\{ \begin{matrix} \text{R} \\ \text{IB} \end{matrix} \right. \;\vdots\; \text{Result} = \text{partial lysis}.$$

The following are the details of such an experiment :—

Two series (A and B), of nine tubes, each containing 0·5 c.c. salt solution.

C of guinea-pig M.H.D. = 0·03 c.c., Cd = the same serum heated. Anti-C is the serum (heated at 57° C.) of a rabbit injected with guinea-pig's serum.

Series A. Each tube receives 0·1 c.c. anti-C and 0·1 c.c. Cd.

Series B. To each tube, 0·1 c.c. anti-C alone is added.

All the tubes are placed in the incubator for an hour at 37° C.

To the several tubes of both series alike are then added increasing amounts of C, viz., 0·03, 0·04, 0·05 c.c., etc. Incubation for another hour. To each tube the standard amount of red corpuscles treated with IB is then added, and the tubes are incubated for another hour.

The results are shown in the following table :—

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Amount of C added in c.c. ..	0·03	0·04	0·05	0·06	0·08	0·1	0·12	0·14	0·16	0·18
Series A— **Amount of lysis in added corpuscles**	0·78	0·88	0·9	Almost complete			Complete			
Series B, ditto...	0·1	0·55	0·62	0·7	0·77	0·80	0·88	Almost complete		Complete

The effect of Cd in preventing the combination of C is thus seen throughout. If we take the first tube, it is seen that the previous addition of 0·1 c.c. Cd has kept out sufficient C to produce lysis of 0·68 of the added corpuscles, *i.e.*, about 0·02 c.c. C.

On the Amount of Complementoid derived from Complement.

We have seen that the evidence for the existence of complementoid is supplied by its preventing complement from combining with certain molecules (R + IB and anti-C respectively). The amount of complementoid present may be measured by the amount of complement which is thus kept out of combination. Thus, if each molecule of complement gives rise to one molecule of complementoid, then 0·1 c.c. of heated serum (Cd) should prevent the combination of the complement in 0·1 c.c. of the same serum unheated, provided, however, that the complement cannot displace the complementoid after it has combined. Suppose we wish to estimate how much complement will be kept out by a given amount of complementoid, we proceed as follows. Two series of tubes (A and B) are taken, and to each tube is added the same amount of IB (say four doses); lysis is produced in all the tubes by a dose of C. To each tube in series A a given amount of Cd is added, and 1 hour at 37° C. is allowed for combination. We then add increasing amounts of C to the tubes in each series, and find, by the method described above, how much C is taken up in the two series. The difference between the amounts in the two series gives, of course, the amount of C which has been prevented from combining by the Cd used. We can in the same way compare the amount of guinea-pig's C, kept out by a given amount of rabbit's C and Cd respectively, and the amount of rabbit's C kept out by guinea-pig's C and Cd. Of course, in every experiment of this kind, the Cd is a heated portion of the same C as that used for comparison.

A considerable number of experiments of this kind have been performed both with rabbit's and guinea-pig's complementoids, and differences are found in the two cases. In five experiments in which rabbit's complementoid was used, it was found that there was kept out of combination a quantity of complement, approximately equal to the amount of complementoid used. In the case of the guinea-pig's complement, on the other hand, the amount of complement kept out was always distinctly less; on the average, 0·6 c.c. of C corresponded to 1 c.c. of complementoid. We may therefore say that a molecule of rabbit's C gives rise to a molecule of Cd, which has an affinity for the R + IB molecules after lysis, practically equal to that of C; whereas, with the guinea-pig, in the process of heating, either some of the C becomes entirely destroyed, or the Cd formed has a lower combining affinity, and some of it can be displaced by C.

On the Relative Firmness of Union of C and Cd respectively with R + IB Molecules after Lysis.

To determine this, we have compared in the usual way the amount of unaltered C which can be taken up, with the amount of a mixture of C and Cd in equal parts. If the C and Cd molecules have the same combining power, it is evident that the saturation of the R + IB molecules will occur after the addition of the same amounts in the two cases. After the saturation point has been reached, however, twice as much of the C + Cd mixture as of the undiluted C would have to be added before a free dose of C would be obtained. As a matter of fact, this is pretty much what happens.

The following may be taken as examples :—

I. Two series of tubes, A and B, 3D of IB added to each tube, and lysis is produced in all by 1D of C = 0·05 c.c. C is then added in increasing amounts.

A.

	1.	2.	3.	4.	5.	6.	7.
Amount of C added in c.c.…	0·1	0·15	0·2	0·25	0·3	0·35	0·4
Amount of C left over…..	0	0	trace	much	1D +	1D +	1D +
				B.			
Amount of C and Cd mixed in equal parts……….	0·1	0·15	0·2	0·25	0·3	0·35	0·4
Amount of C left over…..	0	0	first trace	trace	more	1D −	1D +

II. 5D of IB to each tube. M.H.D. of C = 0·03.

A.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Amount of C added in c.c.	0·08	0·12	0·16	0·2	0·24	0·28	0·32	0·36	0·4
Amount of C left over in doses……………	0	0	0·65D	1D +	1D +	1D +	1D +	1D +	1D +
					B.				
Amount of mixture of C and Cd, equal parts added………….	0·08	0·12	0·16	0·2	0·24	0·28	0·32	0·36	—
Amount of C left over in doses……………	0	0	0·17D	0·65D	1D +	1D +	1D +	1D +	—

It appears from these examples that the points at which free C appears in the two cases ((*a*), where pure C is used, and (*b*) where a mixture of C and Cd in equal parts is used) approximately correspond —only a little more of the mixture of C and Cd has to be added before saturation of the R + IB molecules occurs. It is also seen that, after the saturation point has been reached, fully twice as much of the mixture as of pure C has to be added before a free dose of C is obtained. Of course, if the C molecules had a much greater affinity than the Cd molecules, the *actual* amount of C added would be approximately the same in the two instances. This, however, is very far from being the case. In other experiments we have found, when lysis is produced first, then a small quantity of Cd added and allowed to combine, and then increasing amounts of C, that the surplus C appears to come off less sharply than when C alone has been added. This would appear to indicate that a certain amount of Cd is displaced by C; it must, however, be a small amount.

We may therefore conclude that the C and Cd have *approximately the same* combining affinity for the R+IB molecules after lysis. If there is a difference in favour of the energy of combination of the former, it is a slight one.

On the Relative Firmness of Union of C and Cd with Anti-C.

Here the mode of procedure is of the same nature. A given amount of anti-C is added to salt solution in two series of tubes. To the A tubes increasing amounts of pure C are added; to the B tubes the same amounts of a mixture of C and Cd in equal parts. One and a-half hours at 37° C. are allowed for combination, and then red corpuscles treated with IB are added to each tube to find how much C is obtainable.

Examples:—

1.—0·1 c.c. anti-C in each tube.

A.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Amount of C added in c.c.	0·04	0·05	0·06	0·07	0·08	0·09	0·1	0·12	0·14	0·16	0·18
Amount of C obtainable from the mixture in doses (D)...	0	0	0	first trace	0·12	0·27	0·27	0·4	0·73	0·82	0·88

B.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Amount of C and Cd in equal parts added	0·04	0·05	0·06	0·07	0·08	0·09	0·1	0·12	0·14	0·16	0·18
Amount of C obtainable	0	0	0	0	0	first trace	0·15	x*	0·8	0·55	0·68

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* This tube was accidentally broken.

2.—0·05 c.c. anti-C in each tube.

A.

	1.	2.	3.	4.	4.	5.	7.	8.	9.	10.
Amount of C added in c.c. ..	0·03	0·04	0·05	0·06	0·07	0·08	0·09	0·1	0·12	0·14
Amount of C obtainable, in doses (D)	0·09	0·12	0·4	0·48	0·65	0·73	0·9	1·0	1+	1+
B.										
Amount of C and Cd in equal parts added ...	0·05	0·06	0·07	0·09	0·1	0·12	0·14	0·16	0·18	0·2
Amount of C obtainable	0·05	0·15	0·28	0·4	0·5	0·73	0·88	1	1+	1+

In this case of course, as already explained, the surplus C comes off much more gradually, and a more accurate result might be expected. The theoretical consideration of all the factors, however, is one of much complexity, and we do not claim to explain it fully. The following points are to be noted however:—(1) The amount of C obtainable has been estimated by the amount of lysis—the two, however, only approximately correspond—it is not possible to detect the smallest amount of C, we can only note the first appreciable lysis; (2) as has been stated, the combining value of C (fresh serum) usually falls somewhat when converted into Cd. (Unfortunately a separate estimation of the exact value of Cd in the experiments before us was not made); (3) when there is a surplus of C and Cd molecules the former are taken up by the intact corpuscles treated with IB, the latter not at all; the balance of dissociation may thus be affected.

Looking, however, at the results in a general way, we see that C is kept out of combination by Cd, that the points at which surplus C is obtained are not far distant from each other in the two series, and that the interval from the point at which C is first obtainable to that at which a full dose is got is much lengthened in series B, though it is not quite doubled. If we take the tube in series B (mixture of C and Cd added), which gives a third lysis in the added corpuscles, we find that the corresponding tube in series A (C alone added) gives about two-thirds lysis. We may thus conclude that with anti-C also the firmness of union of Cd does not differ greatly from that of C.

On the Union of Complementoid with R + IB Molecules before Lysis.

As has been mentioned above, the addition of complementoid to red corpuscles treated with IB does not prevent the subsequent action of complement and the production of lysis. This may be due either (*a*) to complementoid failing to combine with the R + IB molecules, or (*b*) to its being displaced by complement after it has combined; both factors may be partly concerned. There are two methods by which the question may be investigated, and we have carried out both of them.

In the first place we may add a given amount of heated serum (Cd) to red corpuscles treated with IB, allow time for combination, then remove the fluid by centrifugalisation, and then test the amount of Cd present in the fluid by finding how much C it will prevent from combining with R + IB molecules after lysis. We shall call the Cd treated in this way Cdx. A control is made with the same amount of heated serum (Cd) which has not been in contact with red corpuscles treated with IB. We have performed a number of experiments of this kind, and the result has always been to show that only a fraction of the Cd combines with the R + IB molecules. In one experiment it was found that the Cdx of the rabbit kept out two-thirds of the amount of guinea-pig's C kept out by rabbit's Cd, *i.e.*, only one-third of the Cd molecules had combined with the intact red corpuscles treated with IB. With guinea-pig's Cdx, in one case a similar result was obtained, whilst in another a half of the Cd molecules had been removed by combination.

Another method is to bring Cd into contact for a given time with red corpuscles treated with IB (say, 3IB), then to centrifugalise and wash these corpuscles, and then test how much C they will take up. The control will be red corpuscles treated with the same amount of IB, but not with Cd. Similar results emerge from experiments of this kind. The following may be taken as an example:—

Three sets of tubes containing the standard amount of red corpuscles, fully 3D of IB added to each tube.

1. Series A.—We estimate how much guinea-pig's C will be taken up.

2. Series B.—We estimate how much C will be taken up after the addition of 0·04 c.c. Cd (lysis having been first produced).

3. Series C.—The corpuscles are treated with 0·6 c.c. Cd for an hour at 37° C., then centrifugalised and washed to remove the free Cd. We then estimate how much C the corpuscles will take up.

The result is that in—

Series A............	0·175 c.c. of C is taken up.
„ B..........	0·15 „ „ „
„ C............	0·165 „ „ „

In other words, after lysis the addition of 0·04 c.c. of Cd has kept out 0·025 c.c. of C, whereas before lysis the addition of 0·6 c.c. of Cd (fifteen times the amount) has only kept out 0·015 c.c. of C. It is thus seen that a mere fraction of Cd entered into combination with the R + IB molecules before lysis. We may add that the largest amount observed was in an experiment with rabbit's Cd, where it came out that of 0·25 c.c. of Cd added before lysis an amount was taken up equal to 0·1 c.c. of Cd added after lysis.

From all these experiments it is shown that before lysis Cd has a weak affinity for R + IB molecules, and that in any given case only a fraction of the amount added enters into combination. This result is of high importance in connection with the general question as to the action of these substances, since it implies that the action of one substance—complement—increases the combining affinity of another substance—complementoid.

On the Saturation of the R + IB Molecules with Complementoids, after Lysis has occurred.

Seeing that red corpuscles treated with multiple hæmolytic doses of IB take up multiple doses of C, we may produce lysis by a single dose of C, and then find whether the affinities of the remaining R + IB molecules can be satisfied with Cd. The different stages of such experiments are (*a*) The addition of several doses of IB to the corpuscles, time being allowed for combination; (*b*) Lysis by a single dose of C; (*c*) The addition of Cd in excess; 2 hours at 37° C. are allowed for combination; (*d*) The addition of about one dose of C; 1 hour at 37° C. for combination; (*e*) The addition of red corpuscles treated with IB to test for the presence of free C. (In case the hæmolytic value of C should fall during the experiment, the same amount of C as that used in (*d*) should be added to a little salt solution and placed in the incubator at the same time for an hour; its value is then tested by adding red corpuscles treated with IB.) We can in this way test the saturating power of rabbit's or guinea-pig's Cd with rabbit's or guinea-pig's C—four possible combinations. A considerable number of experiments of this kind have been carried out, but the general result may be stated that after saturation with Cd not more than a fraction of a dose of the added C has been taken up.

Examples 1 and 2.—*Saturation with Rabbit's Cd.*

Test with Rabbit's and Guinea-pig's C.

M.H.D. of IB = 0·002 c.c.
" guinea-pig's C = 0·045 c.c.
" rabbit's C = 0·11 c.c.

(0·5 c.c. of suspension of red corpuscles is used, so that the doses will be half the amount.)

5D of IB added to 4 tubes, A, B, C, D.

Lysis in all with 0·07 c.c., rabbit's C.

0·6 c.c. rabbit's Cd added to each tube; 2 hours at 37° C., then add

A.	B.	C.	D.
0·065 c.c.	0·09 c.c.	0·03 c.c.	0·05 c.c.
Rabbit's C.		Guinea-pig's C.	

1 hour in incubator.

Add to each the test amount of red corpuscles treated with IB.

The result is that complete lysis of all the added corpuscles occurs. This shows that at most not more than a fifth of a M.H.D. of rabbit's C and not more than a third of a M.H.D. of guinea-pig's C has been taken up.

3. *Saturation with Guinea-pig's Cd.*

Test with Guinea-pig's C.

M.H.D. of guinea-pig's C = 0·04 c.c. (at beginning of experiment), 5D of IB added to 1 c.c. corpuscles, lysis with C and addition of 0·5 c.c. of Cd, 2 hours at 37° C.; 0·06 c.c. of C added, 1 hour at 37° C.; red corpuscles treated with IB added, 1 hour at 37° C. Result, 0·8 of the corpuscles underwent lysis, but in a control with 0·06 c.c. of C alone 0·1 remained undissolved. Here, accordingly, not more than about a tenth of a dose of C entered into combination with the R + IB molecules.

4. *Saturation with Guinea-pig's Cd.*

Test with Rabbit's C.

M.H.D. of guinea-pig's C = 0·07 c.c.

„ rabbit's C = 0·27 c.c.

Three tubes taken containing 1 c.c. suspension of red corpuscles, treated with 6 IB.

Lysis with 0·09 c.c. guinea-pig's C; 1 hour in incubator. Addition of 0·5 c.c., 0·75 c.c. and 1 c.c. of guinea-pig's Cd to the several tubes; 2 hours in incubator.

Addition of 0·3 c.c. rabbit's C; 1 hour for combination.

Addition of the test amount of corpuscles treated with IB. Result in the tube with 0·5 c.c. Cd, two-thirds of the corpuscles underwent lysis; in the other tubes with 0·75 c.c. and 1 c.c. Cd, complete lysis took place. Complete saturation had not occurred with 0·5 c.c. Cd, but with the other amounts it had, so that *at most* about a tenth of a dose of the rabbit's C was taken up.

It is thus seen that it is possible to practically saturate with Cd the surplus R + IB molecules after lysis. Other experiments have indicated that probably a certain amount of Cd is displaced by C added afterwards. But the above results show that when an *excess* of Cd is used, the amount displaced is reduced to a trifling amount.

These results also confirm the result already obtained, namely, that in the case under consideration the haptophore groups of the rabbit's and guinea-pig's complements unite with the same R + IB molecules (*vide supra*).

Conclusions.

The following are the chief results obtained from the experiments described. *It is, of course, to be understood that they are held to* apply only to the cases investigated, viz., the immune-body for ox's corpuscles obtained from the rabbit, used along with rabbit's and guinea-pig's complements and complementoids. Further observations will be necessary to determine whether they obtain generally.

(1) The existence of complementoids in heated sera can be shown in ordinary test-tube experiments, by their preventing (*a*) the union of complement with anti-complement, (*b*) the union of complement with R + IB molecules after lysis.

(2) The amount of complementoid derived from complement, as tested by the combining relationships, varies; in the case of the rabbit it is approximately equal to the original amount of complement; in the case of the guinea-pig it is considerably less than that amount.

(3) The combining affinity of complementoid, both for anti-complement and for R + IB molecules after lysis, is not much inferior to that of complement.

(4) On the other hand, complementoid has a feeble affinity for R + IB molecules before lysis, *i.e.*, for intact red corpuscles treated with immune-body; of the complementoid added only a small quantity enters into combination; hence complementoid does not prevent lysis by complement.

(5) When red corpuscles united with multiple doses of immune-body are lysed by a single dose of complement, the surplus R + IB molecules can be saturated with excess of complementoid, so that almost no complement can subsequently be taken up. This result is obtained also with rabbit's complementoid and guinea-pig's complement, and with guinea-pig's complementoid and rabbit's complement.

"On the General Circulation of the Atmosphere in Middle and Higher Latitudes." By W. N. SHAW, F.R.S., Secretary of the Meteorological Council. Received May 16,—Read June 2, 1904.

In the course of an investigation into the trajectories, or actual paths of air, by means of synoptic charts, which is still in progress,* it became apparent that the paths of air taking part in cyclonic disturbances near the British Isles when traced backward did not always originate in anti-cylonic areas, but followed a track skirting the neighbouring high-pressure areas and traversing sometimes a very large part of a belt of the earth in a direction more or less parallel to a line of latitude, and, on the other hand, air moving in the neighbourhood of a cyclonic depression did not invariably seek the nearest barometric minimum, but sometimes passed on, leaving the circulation of the depression on the left hand.

Two suggestions at once arise from these results :—First, that the anti-cyclonic areas of the Atlantic take far less part, as sources of air supply for travelling storms, than is usually attributed to them, and secondly, that the motion of air in middle latitudes is more of the nature of a passage round the pole in a general easterly direction, sometimes from north-west, sometimes from south-west, than is generally supposed.

The evidence in support of these suggestions will be considered when the results of the investigation referred to are presented, but it may be remarked here that the first suggestion, which would indicate that the anti-cyclonic areas are of the nature of stable inert masses of air round which the winds circulate rather than regions out of which winds blow, is not inconsistent with the phenomena of anti-cyclonic weather, and is borne out by the monthly wind charts of the South Atlantic recently prepared by the Meteorological Council, and now in course of publication by the Hydrographic Office of the Admiralty; and further that the existence of a general circulation of the atmosphere from west to east along middle latitudes right round the earth, diverted to the northward along the eastern sides of the oceans and back again to the southward across the land areas, is supported by the recent summary of cloud observations by Hildebrandsson.† It is also supported by the isobaric distribution for the 4000 metre level computed by Teisserenc de Bort, with which the observed motions of the upper clouds are in agreement.

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* Some of the results of this investigation have been already published, 'Quarterly Journal Roy. Met. Soc.,' vol. 29, p. 233, and vol. 30, p. 57; 'Monthly Pilot Chart of the North Atlantic and Mediterranean,' February, 1904.

† 'Rapport sur les Observations Internationales des Nuages au Comité International Météorologique,' also 'Brit. Assoc. Report,' Southport meeting, 1903.

It is the second suggestion, the general circulation in middle latitudes round the pole, with which the present paper deals.

I propose to refer to certain representations of the average distribution of pressure and the corresponding average winds for January. It may be conceded at once that the motion of air represented by any synoptic chart of a considerable part of the earth's surface in middle or higher latitudes, including ocean areas, for any day in January could not by any stretch of the imagination be regarded as a "steady" motion round the polar axis. The conspicuous features are large cyclonic systems travelling irregularly, and the actual motion is exceedingly complicated. The chart of mean isobars for the month, fig. 1, displays a large area of low pressure over the North Atlantic, south-east of Greenland, the axis of which lies along the path frequently followed by centres of depressions, and indicates prevailing westerly winds on the southern side of the low pressure and prevailing easterly winds on the northern side.

But it is also well known that the cyclical distribution of isobars round local centres and corresponding rotatory winds are specially characteristic of the surface as distinguished from the upper air. For a section taken at successively higher levels the pressure diminishes more rapidly over cold areas than over warm areas, because the air, to the weight of which the pressure at the base of the stratum is due, is denser in cold regions than in warm ones. The turbulent character of the motion is moderated as higher levels are reached, and its rotatory character may be lost at a sufficient height.*

In general accordance with the obliteration of cyclical motion at great height the system of isobars computed by Teisserenc de Bort for the 4000 metre level, fig. 2, shows no isolated low pressure areas, and the lines suggest a circum-polar circulation instead of the system of local cyclonic circulations. The isobars are deflected in certain parts from the lines of latitude, but they form complete circum-polar rings. It is not unreasonable therefore to regard the actual motion at that level on any day as the result of disturbances of "steady" motion, the steady motion, about which the actual motion fluctuates, being represented by flow along the mean monthly isobars.

Since two consecutive isobars are not strictly speaking parallel to each other throughout their course, but diverge in some regions and converge in others the velocity is different at different points of an isobar. Upon the principles of hydrodynamics the change of velocity, in the absence of any impressed force to produce such a change, implies an alteration of pressure; hence, where the isobars are widening, the

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* See Hann, 'Meteorologie,' p. 538, and Teisserenc de Bort, 'Brit. Assoc. Report,' 1903.

FIGURE 1. SURFACE ISOBARS FOR JANUARY.
REPRODUCED FROM HANN'S "METEOROLOGIE."

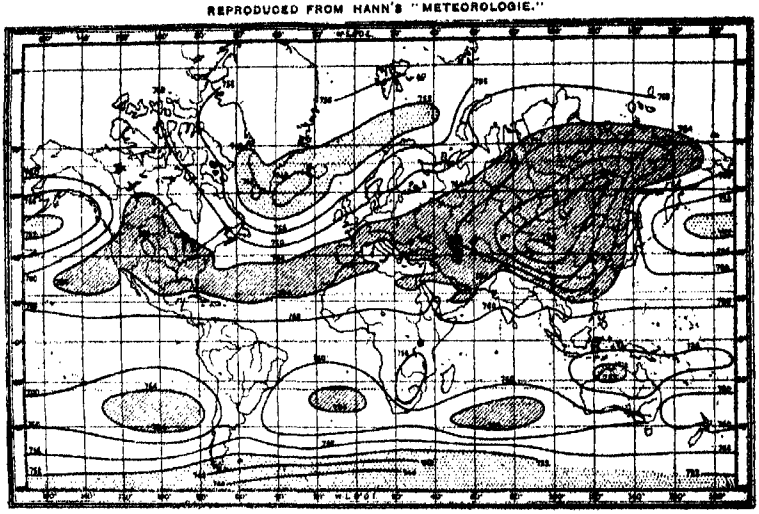
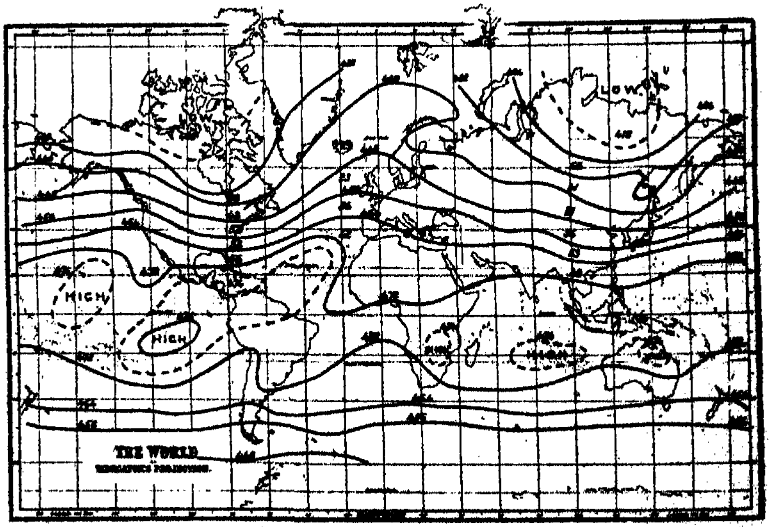


FIGURE 2. ISOBARS AT THE LEVEL OF 4000 METRES FOR JANUARY.
FROM HANN'S REPRODUCTION OF THE ORIGINAL DIAGRAM BY TEISSERENC DE BORT.



Pressures in millimetres: Velocities in miles per hour, corresponding to the acceleration for different gradients resulting from the Earth's rotation.

FIGURE 3. MEAN PRESSURE DUE TO THE WEIGHT OF THE STRATUM OF THE ATMOSPHERE BELOW 4000 METRES.
FOR THE MONTH OF JANUARY. COMPUTED FROM FIGURES 1 AND 2.
PRESSURES ARE GIVEN IN MILLIMETRES.

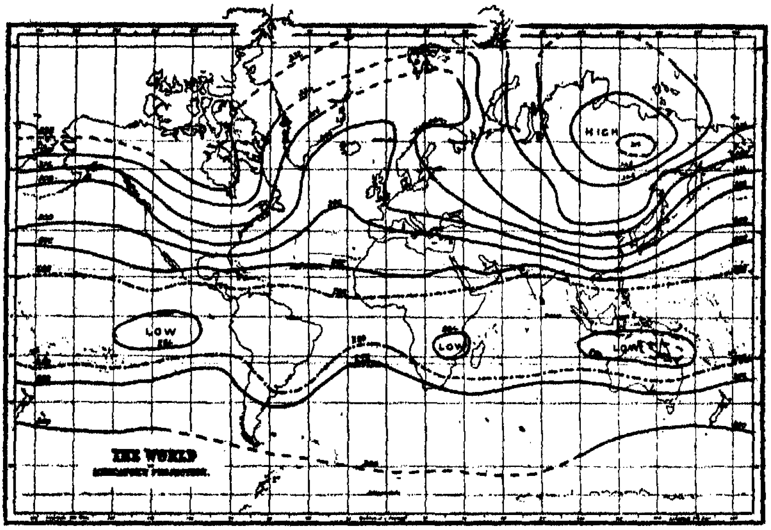
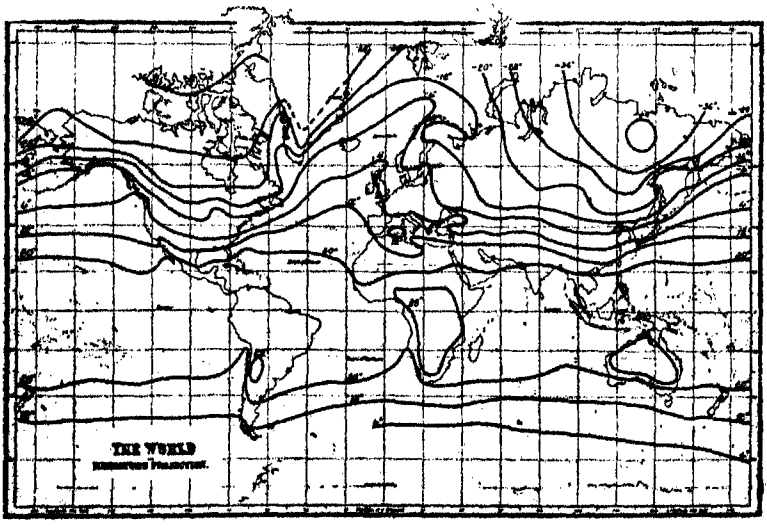


FIGURE 4. MEAN TEMPERATURE AT THE EARTH'S SURFACE.
FOR THE MONTH OF JANUARY. IN CENTIGRADE DEGREES.



flow of air must diverge from strict parallelism with the isobar towards the region of higher pressure, and *vice versâ*. The angle of divergence at any point would be, however, too small to affect the considerations put forward in this paper.

Neglecting the effect of frictional resistance, the condition of persistent motion along parallel isobars is that the force due to the distribution of pressure, *i.e.*, the pressure gradient, shall supply the acceleration which is necessary to keep a particle of air in its path; this condition is expressed by the relation between the pressure gradient γ, expressed in inches of mercury per degree (60 nautical miles), and the velocity V of the moving air in statute miles per hour, as follows:—

$$\gamma = \mathrm{D}\,(\mathrm{V}^2 \cot\rho \times 0\cdot000016 + \mathrm{V}\sin\lambda \times 0\cdot033),$$

where λ is the latitude, ρ the angular radius of the small circle osculating the path, and D the density of the moving air in pounds per cubic foot.

Of these two terms, that containing ρ depends upon the curvature of the path and, from the magnitude of the numerical coefficient, it is clearly insignificant unless the velocity of the wind is very great or the radius of curvature of the path very small. It becomes very important in the case of revolving storms of small diameter. The other term is that depending upon the rotation of the earth, and represents $2\omega\mathrm{V}\sin\lambda$,* where ω is the angular velocity of the earth's rotation. Omitting the first term we get for the condition of steady motion

$$\gamma = \mathrm{DV}\sin\lambda \times 0\cdot0330 \text{ inches per degree of 60 nautical miles.}$$

On fig. 2 the gradient is already indicated by the separation of the isobars, the pressures being noted on the diagram in millimetres; the wind velocity which is necessary for steady motion, assuming, for the purpose of computing D, a fixed vertical temperature gradient, and neglecting the effect of the divergence or convergence of the isobars, is given in figures in various parts of the diagram. The velocities here indicated refer to the air at the 4000 metre level, but it may be noticed that since the pressure gradient for a given velocity is proportional to the air density, and the pressure is due to the weight of the superincumbent air, steady motion along parallel isobaric lines with the same velocity at all altitudes would result, if the run of the isobaric lines were the same at every altitude. That condition would be satisfied if at each altitude the isobars were also isothermal lines.

The wind velocity near the surface is diminished by surface friction, but it follows from this relation between gradient and velocity that beyond the range of appreciable surface friction the velocity does not increase with height in an atmosphere in which the distribution of isobaric lines is similar at all heights.

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* See Hann, 'Meteorologie,' p. 421.

The velocities entered upon the diagram lie between 20 and 66 miles per hour, and these are not inconsistent with observed cloud velocities, so that a steady motion with the velocities indicated is a reasonable representation of the average conditions so far as they are known. As regards the direction of the slope of pressure, that direction is determined by the relation of the direction of motion of the air to the direction of rotation of the earth. Whatever be the direction of motion of the air, the horizontal acceleration arising from the earth's rotation is along the normal to the path, and to the left, in the northern hemisphere. On that side, therefore, the low pressure must lie. For motion along a parallel of latitude the slope of pressure will be "downward" towards the pole for motion from west to east, and for motion from east to west "downward" towards the equator.

Hence we may conclude that the distribution of pressure at the 4000 metre level is favourable for a steady circulation of air round the polar axis, with an average velocity of about 50 miles per hour. The direction of the motion is from west to east, with divergence in the northern hemisphere towards the north over the Pacific and Atlantic oceans, and back again to the south over the Continental land areas. In the southern hemisphere the motion follows the lines of latitude more closely and the deflections are less marked, though the influences of the land projections are similar.

Below the 4000 metre level is a region of cyclonic depressions with rotatory motion, lying between the tropical high-pressure belt and other anticyclonic regions to be found in the far north. The motion near the surface level corresponds with the surface distribution of pressure, which is made up of the distribution at the 4000 metre level, transmitted to the surface, and the pressure due to the weight of the stratum below the 4000 metre level. I now exhibit (fig. 3) the distribution of this remainder of the surface pressure when the distribution at the 4000 metre level has been deducted. It has been obtained by plotting the difference between the surface distribution of fig. 1, and Teisserenc de Bort's distribution at the 4000 metre level, fig. 2.

The result is very remarkable. A comparison of figs. 2 and 3 shows at once that the general trend of the lines is very similar to that for the upper air but the *direction of the gradient is reversed.* This is in accord with the theoretical calculation of the direction of the gradient, because the direction of motion for such a pressure distribution is the reverse of that represented in fig. 2. *The result of the pressure distribution due to the lower stratum alone would be a circulation round the polar axis from east to west along lines almost identical with the lines of flow for the upper air but in the reverse direction.*

I now refer to fig. 4, showing the average distribution of surface temperature for the same month, January. Again the similarity of the trend of the lines to those of figs. 2 and 3 is obvious. It is of course not in any way remarkable that figs. 3 and 4 should show similar lines, for figure 3 shows the amount of barometric pressure to be deducted from the surface pressure for a layer of air 4000 metres thick, and the calculations of the deductions have been based upon the surface temperatures. The diminution of pressure for a given height is the same at all points of an isothermal line, assuming the vertical temperature gradient to be the same at all points along the line; but that the remainders representing the pressure of the upper atmosphere at 4000 metres should also be very similar in shape, is indeed remarkable, especially when one considers that *the gradient is in the reverse direction* from that of the pressure values for the lower stratum.

It is unnecessary to call special attention to the points of similarity even in detail between the shapes of the "partial" isobars for the lower stratum, fig. 3, and the upper stratum, fig. 2, with reversed gradient. The isolated minima in fig. 3 about the equator, corresponding to isolated maxima in the same regions in fig. 2, are very striking, but one point of difference may be noted. In fig. 2 the circulation indicated is approximately about the geographical pole, where, in consequence, a minimum of pressure is indicated. In fig. 3, the circulation is clearly round a pole of extreme cold in north-east Siberia, where there is a maximum of pressure for the lower air.

It thus appears that the forces represented by the average distribution of pressure for the month of January may be divided into two parts, viz.:—

A, that due to the upper atmosphere, above 4000 metres, which would, if it acted alone, correspond with a steady motion from west to east along paths following closely the lines of the average isotherms; and B, that due to the lower stratum of the atmosphere which, if it acted alone, would correspond with a steady motion also approximately along the isotherms but from east to west.

The actual distribution is represented by the superposition of A and B. Since pressure gradient and velocity are both vector quantities, and are related to each other in simple proportionality, the superposition of force distribution corresponds with the composition of the velocities due to the separate distributions. Hence, in the combination of the two distributions of force at the surface where A is predominant, *i.e.*, in the middle latitudes on either side of the equator, there is a resultant circulation from west to east; where B is predominant, *i.e.*, in higher latitudes, there is a resultant circulation from east to west.

The superposition of the two systems gives a line of minimum pressures, with a westerly flow of air on the equatorial side, and an easterly flow of air on the polar side. It is very irregularly marked in the northern hemisphere, owing to the distance of the pole of cold from the geographical pole; in the southern hemisphere, the arrangement is probably much more symmetrical, owing to the coincidence of the pole of cold with the geographical pole.

The line of minimum average pressure forms the storm track of the circular storms, resulting from the merging of the two circulations. It is evident that such merging must take place. If circumstances were so adjusted that there was an equilibrium condition along any level, the difference of density of air at different temperatures would cause a departure from equilibrium conditions, in one direction above the prescribed level, and in the opposite direction below it. And to this primary cause of disturbance of the steady motions corresponding to the two separate distributions of pressure, must be added the instability, which is due to the condensation of water vapour. The region of minimum pressure becomes, therefore, the scene of great changes of energy, cyclonic circulations, and variable winds. It may, indeed, be noticed that increase of entropy when mixing takes place, is represented by $\frac{H(T-T')}{2TT'}$ (supposing $T-T'$ to be small compared with T or T'), where H is the quantity of heat transferred in mixing, and T and T' are the absolute temperatures of the amounts of air, supposed equal, which mix. Hence the entropy change is greatest where there is the greatest temperature difference, but, for the same temperature difference, where temperatures are lowest.

To sum up the result that has been arrived at, the average distribution of pressure can be divided into two parts, neither of which shows the characteristics of local cyclonic distribution; one part, due to the upper atmosphere, favours a westerly circulation, the other, due to the lower atmosphere, favours an easterly circulation, and both circulations follow roughly the lines of the average isotherms.

This result leads to many suggestions of considerable importance. The second component of the distribution is obviously directly dependent upon surface temperature, and must be changed when surface temperature changes; the first may also be regarded as depending ultimately upon surface temperature, for its lines follow those of surface temperature on the average, but the connection must be less direct. It may possibly indicate differences of thickness of the atmospheric layer as distinguished from differences of density in a layer of uniform thickness. The first effect of a change in the distribution of surface temperature will be to change the character of the second component, leaving the first component unchanged, except in so far as expansion of air in the lower strata alters the pressure at a given level in the upper strata. The study of the effects of recognised changes of temperature distribution upon the second component, which are easily calculable, may have very important consequences in relation to classifying the facts within our knowledge of weather changes in middle latitudes. It seems to follow directly that easterly winds are, as a rule, winds of relatively speaking low altitudes, due to surface temperature, and that local areas of high pressure, with an anti-cyclonic circulation, may lie underneath regions of general westerly flow in the upper air.

Another conclusion that follows directly from this method of analysis of the distribution of forces corresponding to the surface circulation, is the confirmation that it affords of the suggestion of the existence of a high-pressure area over the Antarctic Continent, made by Sir J. Murray, in the discussion of the "Challenger" observations. Such indications of the results of Antarctic explorations as have been already received are consistent with the suggestion,* and the detailed results of the recent expeditions must furnish very valuable additions to the material for the study of this interesting question. It is clear that the effect of the component, due to the lower atmosphere in the southern latitudes, will become intensified where the intensity of the low temperatures becomes effective; and the pole of extreme cold, which in the southern hemisphere must be nearly coincident with the geographical pole, will have associated with it a component distribution for easterly circulation similar to the low-temperature pole of north-east Siberia, in the northern hemisphere. The intensity of the cold in the south polar regions is undoubted, and the existence of the distribution for an easterly circulation round a high-pressure centre, due to the weight of the lower air, follows directly therefrom.

A third effect of the distribution of pressure in lower regions of the atmosphere, and the corresponding air circulation, may perhaps be traced in the series of wind charts of the South Atlantic already referred to, where there is obvious evidence of a tendency of the winds to run tangentially to the coast line. The coast line is equally obviously a line of separation between regions of different surface temperature distribution, and hence a locality of steep temperature gradient. Thence follows a steep pressure gradient for the lower atmosphere, and associated therewith a distribution favourable for the flow of air in opposite senses on the two coast lines for the same latitude.

The division of the atmosphere into an upper and a lower stratum at the 4000 metre level is perfectly arbitrary, and that level is only chosen because M. Teisserenc de Bort selected it for constructing his charts of mean isobars of the upper air 18 years ago.† It is in the region of the clouds of intermediate height and probably does not correspond with any specific discontinuity in the atmospheric layer. It is accordingly remarkable that the separation of the surface, or resultant distribution, into two distributions of opposite type should be so complete when the level of 4000 metres is taken as the surface of separation. It is not desirable to follow out the consequences of small differences that might be found, because the calculation of the isobaric distribution at high levels is itself as yet not susceptible of very great accuracy, and indeed the distribution of pressure at sea level even in the northern hemisphere is not entirely free from uncertainty, owing to the uncertainty of the reduction for altitude.

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* See Mr. Bernacchi's paper on "Winds and Temperature at Cape Adare" in 'Magnetic and Meteorological Observations made by the "Southern Cross" Antarctic Expedition' (published by the Royal Society), pp. 40 and 49.

† 'Annales du Bureau Central Météorologique de France,' 1887, Part 1, p. C1.

The remarks in this paper refer to the circulation in middle and higher latitudes, because the determining force for steady motion is assumed to be dependent upon the velocity of motion of the air and rotation of the earth. The acceleration computed from these elements contains sin λ as a factor, and it is therefore without serious influence in the equatorial regions.

It is fortunate that this is so, because the drift of upper air over the equator is generally accepted as being from east to west, and about 80 miles per hour may be assigned as the rate of this drift. From the results of Sir J. Eliot's work on the cloud observations of India,* it appears that at Simla, in latitude 31° N., the westerly current in the upper air is extraordinarily steady throughout the year, whereas at Madras the upper current shows considerable variation with the season. Between the westerly current at Simla and the easterly equatorial upper current there must be a region where the conditions in the upper air are in many ways similar to the surface conditions in temperate latitudes, that is to say, steady motion would involve the existence of two oppositely directed streams of air at the same level, but in not far distant latitudes. It would appear that for rotatory storms originating in that region the gradient must depend only upon local centrifugal action and the velocities for given barometric variations must be correspondingly great. I am not sufficiently well acquainted with the sequence of events in a tropical hurricane to be able to follow out the suggestion that those phenomena have their origin in the upper air; I hope to be able on a subsequent occasion to cite examples to show that storms in the region of the minimum pressure in temperate latitudes may arise from special *surface conditions*, and there is at least some evidence for the correlative origin of tropical hurricanes.

I have made no comparison of the first results of this method of analysis of the average barometric distribution with the conclusions arrived at by J. Thomson and Ferrel, for the general circulation of the atmosphere, nor with those more recently obtained by Bigelow, because the method of treatment is in some respects novel and it seems desirable to wait for its further application before making any such comparison. I may remark, however, with regard to the theories of the two authors first mentioned, that a steady circulation round the polar regions requires only the supply of the comparatively small amount of energy necessary to make up the loss occasioned by surface friction, and *consequently no great transference of energy from the* equatorial regions to middle or higher latitudes in the form of heat or otherwise is demanded for the maintenance of the circulation.

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* 'Indian Meteorological Memoirs,' vol. 15, Part I, 1903.

Moreover, I have confined my observations to the barometric distributions for the month of January. So far as I have examined the distributions for July, the conclusions to be drawn from them are in many respects similar, but the separation of the pressure component for easterly circulation from that for westerly is not complete at the 4000 metre level as it is in the case of January.

In conclusion, I desire to acknowledge the assistance I have received from Mr. G. T. Bennett, M.A., of Emmanuel College, Cambridge, with whom I have discussed especially the dynamical questions involved, and from Mr. R. G. K. Lempfert, M.A., and other members of the staff of the Meteorological Office, who have supplied me with much of the material upon which the general conclusions set out in this paper have been based.

"On the Structure and Affinities of Palæodiscus and Agelacrinus."

By W. K. SPENCER, B.A., F.G.S., Burdett Coutts Scholar, University of Oxford. Communicated by Professor W. J. SOLLAS, F.R.S. Received March 22,—Read June 9, 1904.

[PLATE 1.]

The following research was undertaken at the suggestion of Professor Sollas. It endeavours to elucidate, by the aid of the method described in the 'Phil. Trans.,' B., vol. 196, the structure of two genera of rare but very important Palæozoic Echinodermata, namely, the Echinoid Palæodiscus and the Edrioasteroid Agelacrinus. The fossils were ground at uniform distances of $\frac{1}{10}$ mm., and each successive surface photographed. From tracings of the photographs wax models were constructed. On the results of these investigations views are brought forward as to the relationships of some of the groups of the Echinodermata. I have to thank Professor Sollas for his never-failing advice and assistance, and also Dr. Bather for his courtesy in my visits to the British Museum of Natural History.

Palæodiscus ferox (Salter).

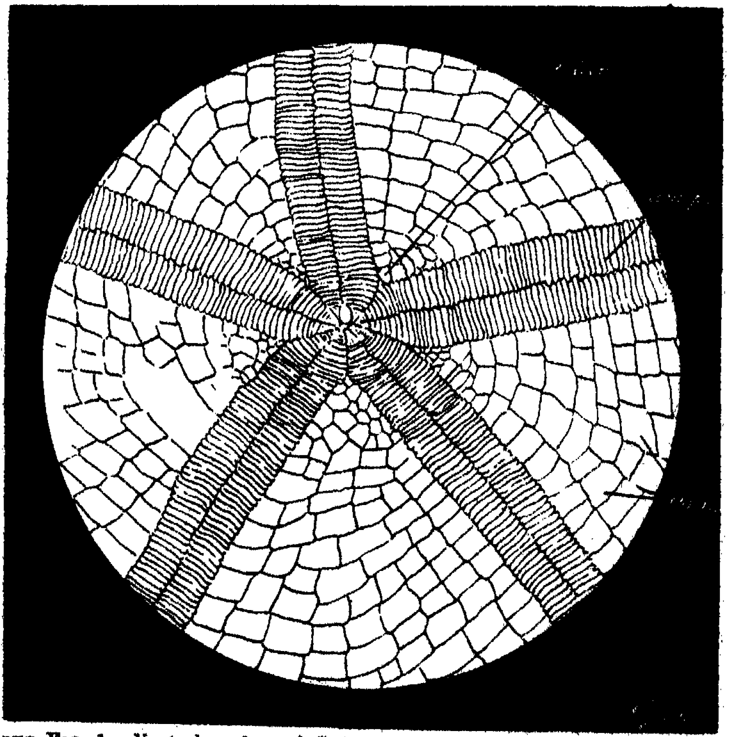
Palæodiscus was discovered by Salter (1) in the Lower Ludlow beds at Leintwardine, Shropshire. The specimen was in the form of a cast, and otherwise imperfect. Salter was unable to decide whether "it was an Ophiurid with contracted arm plates or one of the Asteriadæ with a greatly developed masticatory apparatus."

Wyville Thomson (22) in 1861 described specimens contained in the College Museum in Belfast. He placed Palæodiscus in near relationship with Echinocystites, a genus which he here describes for the first time. Both genera were recognised as Echinoids, but with close relationships to the Cystoids. Wright in his monograph of the 'British Fossil Echinodermata of the Oolitic Formations' was apparently unaware of Wyville Thomson's work, and merely copies Salter's descriptions. Zittel, in 1879, while recognising the Echinoid affinities of Echinocystites, yet places Palæodiscus amongst the Asteroidea. Neumayr, in 1881, regarded Palæodiscus and Echinocystites as very nearly related. "Im Ganzen stellt Palæodiscus einen Typus vor, welcher Charaktere von Seesternen mit solchen von Cystocidaris (Echinocystites), der wichtigen Zwischenform zwischen Seeigeln und Cystideen, verbindet." (16, p. 419.)

Gregory (5, p. 130), in 1897, definitely placed Palæodiscus amongst the Echinoids. He remarks, "the general characters of the skeleton are more echinoid than asteroid; the absence of special adambulacral plates, the occurrence of small articulating spines, the resemblance of the interradial perisomatic plates to those of Echinocystis, and the characters of the masticatory apparatus, are all points which ally Palæodiscus to the Echinoidea, and separate it from the Stelleroidea." On two other points, however, his description is by no means so accurate, for he says that the ambulacral plates are flush with those of the interradii, and the ambulacral plates are not perforated by pores, but the podia pass out between the plates.

The most perfect specimens of *Palæodiscus ferox* discovered up to the present are in the Grindrod collections of the Oxford University Museum. Using these as his material, Professor Sollas, in 1900, gave a description of the ambulacra and the lantern of Aristotle. All the specimens except one were in the form of casts. By the aid of these casts and a well-preserved ambulacrum two series of plates in the ambulacra were identified, an outer series, pierced for podia, and an inner series.

Professor Sollas (20, p. 705) called the outer series the true Echinoid



TEXT FIG. 1.—Ventral surface of *Palæodiscus ferox* reconstructed from several specimens in the Oxford Museum; *i.iap.*, initial interambulacral plate; *am.p.*, ambulacral plates; *rh.p.*, rhomboidal plates of interambulacral areas.

plates, the inner he compared to the ambulacral ossicles of Asteroids. This suggested a solution as to the long-standing puzzle of the relationships of Asteroids and Echinoids. One specimen of Palæodiscus showed plates in the vicinity of the mouth which had fortunately escaped solution. That no doubt might remain as to the existence of the double series of plates, one of the ambulacra of this specimen was cut away and ground. The result of the investigation, together with some amplifications in the description of the genus, form the first part of this paper.

Description.—The general appearance of the form of Palæodiscus, as preserved in the shale, suggests that it was originally discoid and rounded. All the known remains are flattened almost completely in the horizontal plane, and are thus quite different from the impressions of the globular Echinocystis, which lie in almost any plane. (Plate 1, fig. 1.) Usually the peristomal region is occupied by a cast of the lantern of Aristotle. One of the specimens as described by Professor Sollas possesses, however, an impression of the peristome, which is seen to be occupied by the plates of the ambulacra. No interambulacral plates are present here. This is the first of the many embryonic and primitive characters which characterise the genus. It recalls the arrangement which occurs in certain other families of the Palæchinoidea, namely, the Bothriocidaroida, the Lepidocentridæ and the Lepidesthidæ. Further, Professor Lovén (11, pp. 6, 7, 12) has shown that in the young stages of Goniocidaris and Strongylocentrus the ambulacral areas meet and shut out the interambulacral plates from the mouth region, although later these latter plates invade the peristome.

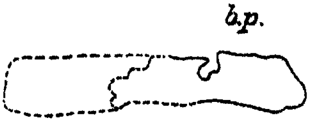
The interambulacrum, as shown in fig. 2, begins with a single plate. This acquires great importance from the studies of Lovén and Jackson. Lovén (11, p. 12) has shown that in the interambulacrum of young Echinoids there is but a single plate. During later growth the initial plate is gradually resorbed. The initial plate is represented, however, in the adult clypeastroids and spatangoids as also in the Palæozoic genera Melonites, Lepidechinus, and Pholidocidaris. There is one genus of Palæozoic Echinoid—Bothriocidaris—which possesses only one row of plates in the interambulacral regions. This has led Jackson (9, p. 233) to suggest that Bothriocidaris represents an ancestral form from which the remaining Echinoids may be derived. The form of the inter-ambulacral plates of Palæodiscus as detailed below shows, however, that even if we take the criterion of the interambulacrum, it appears much more primitive and ancestral than that of Bothriocidaris. The majority of the interambulacral plates are rhomboidal in form, and it is only near the peristome that they become polygonal. Lovén (11, p. 20) shows that the newer interambulacral plates arise distally from the mouth, and are nearly quadrangular. Later they become polygonal owing to growth pressure. Jackson (9, pp. 225, 228, etc.) in his studies of Palæozoic Echinoids shows that various genera of these also possess rhomboidal inter-ambulacral plates distally, but these rapidly become polygonal.

Palæodiscus, with its great number of rhomboidal interambulacral plates, shows in this, as in all other respects, very primitive features. The plates are in several rows radiating from the initial plate in a fan-shaped manner (fig. 1). It is this arrangement we must regard as ancestral. The general Asteroid appearance is very suggestive.

Both interambulacral and ambulacral plates are imbricating. The imbrication obeys the general Echinoid rule, namely, the ambulacral plates imbricate adorally, the interambulacral aborally. This imbrication also occurs in the Palæozoic Lepidocentridæ and Lepidesthidæ, as also in the Echinothuridæ. Jackson (9, p. 237) points out that imbrication, since it appears in such widely separated types, is "a variation built upon independent lines."

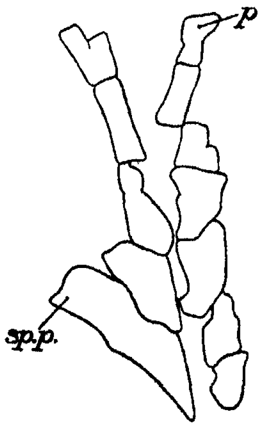
The anus is situated in an interambulacrum, whether on the dorsal or ventral surface it is difficult to say, but certainly at a considerable distance from the apex (Plate 1, fig. 1). This is a position peculiar amongst Echinoids to Palæodiscus, and the closely related genus Echinocystites. It was surrounded by a number of small plates, which gave it a very asteroid appearance. Gregory (5, p. 132) has suggested that the apical plates of Echinoids in general may be derived from the five valvular plates which surround the anus in Echinocystites. The large number of such plates in Palæodiscus cannot be reconciled with this suggestion.

There is no trace of any apical disc in the specimen examined. It has been pointed out that Palæodiscus is always compressed in a horizontal direction, and if an apical plate had existed its remains would have been driven into the impression of the lantern of Aristotle and lost. If the apical disc existed, it did not enclose the anal region either in this form or in Echinocystites. There is no trace of a Madreporite. If we judge from its position in Echinocystites, it would have been situated near to the apex, and is lost for the same reason as would be any apical disc.



TEXT FIG. 2.—*a* Outer ambulacral plate of *Palæodiscus ferox*; dotted lines indicate reconstructed portion put in from cast; *b.p.*, bilobed pore.

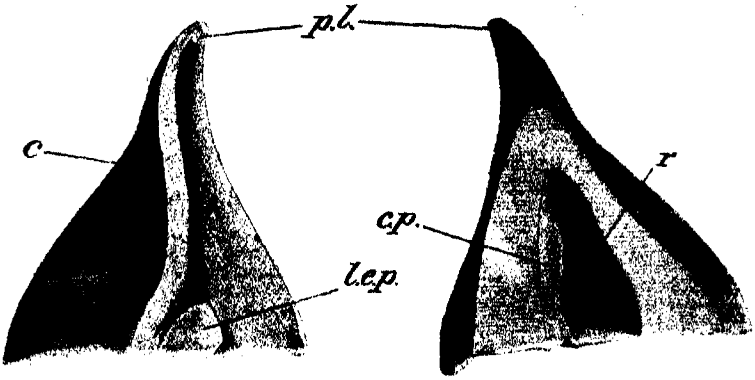
That there were a double series of plates in the ambulacrum had been inferred by Professor Sollas. The outer series consisted of a number of pairs of long thin plates, which alternate irregularly with one another over the middle line. They were pierced by bilobed pores situated at the extreme proximal (mouth) end of the plate, but nevertheless distinctly enclosed by it (fig. 6). The bilobed pore and its marginal position are primitive conditions. Echinoids, I shall attempt to show, must have descended from ancestors (Asteroids) which possessed a single pore passing between the ambulacral plates. The Echinoids more than any other Echinoderm depends for its existence upon the strength of its tube feet. The bifurcation of the tube foot canal by the formation of a double strand of tissue, its arrangement in an arch-like manner, and its enclosure in the plate would strengthen the power of the tube foot considerably. Palæodiscus shows the beginnings of these characters. The inner series of these plates in the cast are observed to dip downwards and distally. They lie in a groove which is partially filled in with sandstone. The existence of both inner and outer series of plates is confirmed by the series of sections taken. An examination of the specimen showed that the outer series of plates have suffered much from solution, but are fortunately best preserved over the ambulacral groove, probably because of the greater mass of calcite in this region. In the series of sections taken the outer series were visible from 1—7, showing that they had a thickness of $\frac{7}{40}$ mm. The inner series then appeared, and persisted for $\frac{1}{4}$ mm. The outer plates were pressed down over the inner series so that little trace of an ambulacral groove appeared. It is this displacement combined with solution which has in ill-preserved specimens, and these are the majority, left little or no trace of a distinct inner series. The evidence of the behaviour of the inner series in the mouth region was quite conclusive, however, as to their individuality. Here they separate out just as do the ambulacral ossicles forming the mouth of the skeleton of Asteroids. This



TEXT FIG. 3.—Inner ambulacral plates of same; *p.*, plates in mouth region separating from each other; *sp.p.*, splayed out portions of plates.

separation, which is quite distinct, causes the inner series to occupy a position which is incompatible with the view that they are the inturned edges of the outer series of the ambulacral plates.

Traces of the aboral ambulacrum may be seen squeezed through on to the ventral surface. The ambulacral plates in this region as noticed by Gregory appear much narrower than those of the ventral surface.



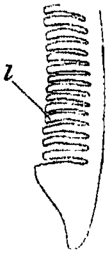
Inner View *Outer View.*

Text Figs. 4 and 5.—Portions of Half Pyramid of *Palæodiscus ferox*. Fig. 4, internal view, *p.l.*, *processus labialis*; *l.e.p.*, *lineæ eminentes pyramidales*; *c.*, cut away portion of pyramid. Fig. 5, external view; *c.p.*, concave outer surface; *r.*, ridges on pyramid.

In two of the inter-radii examined were portions of pyramids. It was found possible to reconstruct the proximal portion of one of these. The lateral surfaces still preserved the ridges which served for the attachment of the interpyramidal muscles. They were concave, as they are in the young Echinoid (Lovén 11), and thus present another of the embryonic features so peculiar to Palæodiscus. The external surface is deeply cut away. The median elevation forms a well-defined "processus labialis." Towards the proximal end of the exterior surface there is a notch, which is continued distally in the substance of the pyramid. This I cannot find represented in recent Urchins. The "Lineæ eminentes pyramidales" (Val.) are well defined.

The structure of the teeth in recent Echinoid has been described by Giesbrecht. Giesbrecht, from a study of the root end, showed that the wings of the tooth arose by the superposition of lamellæ, which, as the tooth was examined as it approximated to the mouth, became intimately connected by secondary calcification. Lovén (11, p. 9) noticed these lamellæ in the tooth of the very young Echinoid, and also that these lamellar structures soon disappeared, presumably by secondary calcifications. The tooth of Palæodiscus shows embryonic features in the distinctness of lamellæ through by far the greater portion of its substance, and by the absence of secondary calcifications.

Text Fig. 6.



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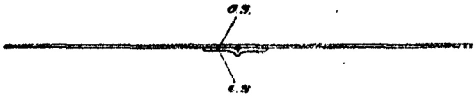
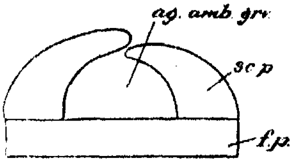


Text Fig. 8.



Text Fig. 6.—Section through tooth of *Palæodiscus ferox*; *l* = lamellæ.

Text Fig. 7.—Diagrammatic reproduction of cross section of an ambulacrum of *Palæodiscus ferox*; *o.s.*, outer series of plates; *i.s.*, inner series.

Text Fig. 8.—Diagrammatic reproduction of cross section of an ambulacrum of a *Lepidodiscus* (*Agelacrinus*) *pileus*; *f.p.*, flooring plate; *sc.p.*, side-covering plate; *ag.amb.gro.* = ambulacral groove.

The carina would seem, as in the other Echinoids, to be formed of dense prisms.

The Edrioasteroidea (*Billings*), *or Thecoidea* (*Jaekel*).

History.—The earliest member of this group to come under notice was a form discovered by Dr. Bigsby in Canada and described by Mr. G. B. Sowerby. Mr. Sowerby compared it to "the arm of an Asterias lying on an Echinoid," but felt himself unable to determine its near affinities.

Forbes, in 1848, described an English specimen of the same group under the name of *Agelacrinites Buchianus.* Forbes remarks, "One important point is strongly suggested by the structure of the arms and arm grooves in this curious genus, viz., that it is possible the ambulacral avenues of all Echinoidæ are embodied arms, when embodied usually separated by ambulacral plates; that here we have the latter, but no avenues, for the arms themselves are the avenues freed from the body, consequently that the anomalous genus Palæechinus (and perhaps Archæocidaris also) is an intermediate form between Agelacrinites and true Urchins, an abnormal Agelacrinites, so to speak, in which the arms have become embodied."

Billings, in 1858, described two species which he calls *Edrioaster Bigsbyi* and *Agelacrinites Dicksoni.* The ambulacral groove of *Edrioaster Bigsbyi* was composed of two series of oblong ossicles. Between the ossicles were said to be ambulacral pores. This structure offers points of resemblance to that of star-fish. Billings himself says, "I have placed *E. Bigsbyi* in the order Asteriadæ because the structure appears to me more like that of the star-fishes than those of the Cystideæ. None of the Cystideæ have ambulacra whose pores penetrate through the covering of the body, and therefore all such genera as Edrioaster Agelacrinites and Hemicystites belong to a very different division of the Echinodermata. When we know more of their structure it is probable they will be arranged as a sub-order for which the name Edrioasteridæ would be appropriate, as it would suggest their sessile condition on the one hand and on the other their affinity to the Asteriadæ." Schmidt, in 1874, in his description of *Mesites Pusireffski* points out the resemblance of Mesites to Edrioaster. He shows that Mesites has a double series of plates, and that between the upper series of covering plates are pores. These, however, lead only into the ambulacral groove which is quite closed from the body cavity. Schmidt on this ground cannot agree that Mesites, at any rate, has any affinities with the Asteridæ.

The theory that Agelacrinus and Mesites were connecting links between the Cystideans and the Eleutherozoa was further advanced by Neumayr. Neumayr (16, p. 420) supports his hypothesis by a statement which he attributes wrongly in "Die Stämme des Thierreiches" to J. Müller. "Wohl weiss man durch die Untersuchungen des grossen Zoologen und Anatomen Johannes Müller, dass in früher Jugend auch bei den Seesternen die Ambulacralcanäle innen liegen, und dass da bei weiterem Wachsthume eine Aenderung in der Art eintritt, dass sich nun erst die definitiven Ambulacral-platten bilden und die Wassergefässe vom Innern abschliessen, währond der sie nach aussen bedeckende Theil resorbirt wird und verschwindet." This double series of plates present in the developing Asteroid is, according to Neumayr, readily capable of interpretation by comparison with the double series of plates in Mesites.

An earlier paper shows that the authority for this statement concerning the developing Asteroid was A. Agassiz. Professor Ludwig has given a very complete account of the development of Asteroids and kindly answering my inquiry categorically denies Agassiz's statement.

Schmidt had already exposed the weak point in this theory, namely, that there are no passages in Mesites which would compare to the ambulacral pores of star-fishes. Mesites has now been definitely relegated to the Diploporite Cystideans. The theory that Edrioaster and Agelacrinus represent the Eleutherozoic ancestor has however survived, and Bather* claims an independent status for this group as definite ancestors of free-moving Echinoderms.

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* 'Treatise on Zoology,' Lankester, vol. 3, "Echinoderma," and in various other papers.

We have seen that Billings demanded pores through the series of ambulacral plates in *E. Bigsbyi*, and Bather has established this fact, as also that there is present an uppermost series of covering plates. This demolishes Jaekel's suggestion (8, p. 45) that the plates through which the pores pass might be covering plates. Whether these pores serve for the passage of ampullæ or podia is an open question and we propose to discuss it in the later portions of this paper. Hall claims to have discovered pores in Agelacrinus. Various authors have, however, with regard both to Agelacrinus and other genera, given accounts which directly contradict the views expressed above.

Roemer, in 1851, obtained a cast of *Agelacrinus rheanus* which led him to surmise that the ambulacral grove was occupied by single flooring plates.

F. B. Meek, 1873, who described a peculiarly preserved specimen of *A. cincinnatiensis* says, "The shell (of the Brachiopod upon which it was sessile) had separated in such a manner as to take with it the under side of the Agelacrinites, and leave its upper side in the matrix so situated as to expose its inner surface. The inner side of each arm or ray is here seen to be composed of a single series of quadrangular pieces that are not imbricating."

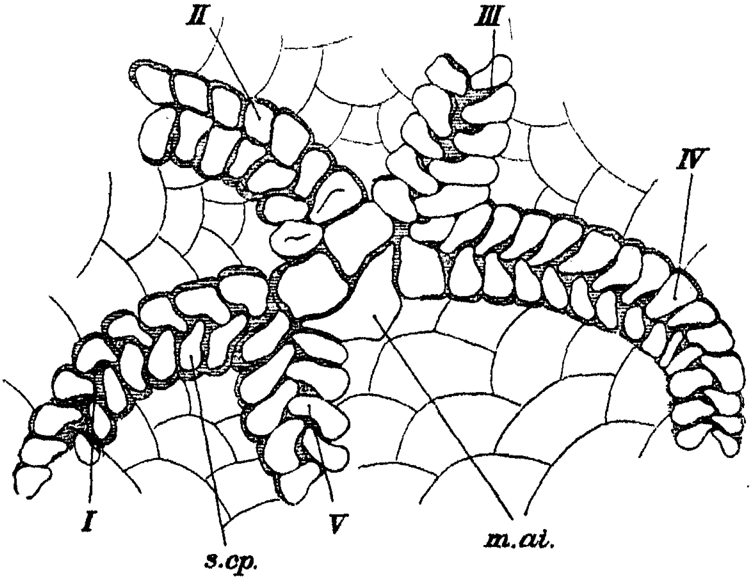
Hemicystis latiuscula, described by Jaekel (8, p. 17) agrees in structure with the above. "Die Rinnen werden hier deutlich unterlagert von einer einfache Reihe querverlängerter etwas winklig vorgezogener Plättchen."

None of these authors discovered in these genera any trace of pores in the ambulacral groove.

Description.—The evidence of the structure of the ambulacra of the Edrioasteroidea, brought forward in this paper, is based upon ground sections through specimens of Agelacrinus, especially through a well-preserved specimen of *Agelacrinus* (*Lepidodiscus*) *pileus* (Hall); as also upon investigations on a uniquely preserved specimen of *Agelacrinus cincinnatiensis* (F. Roemer).

In all cases when the anal pyramid could not be observed, the anal inter-radius was identified from the fact that the rays adjacent to the anus always curve towards it. Following the nomenclature of Jaekel, the ambulacrum to the left of the anus would be called I, and the remainder counted clockwise II, III, IV, V.

Viewed externally the ambulacra of *Lepidodiscus pileus* are seen to be roofed over by an alternating series of plates which are shaped like a bent finger, fig. 9. These do not completely enclose the groove, there being small interspaces between each covering plate. Both longitudinal and transverse section show that these plates also form the sides of the groove. There is no trace of any separate side plates. We may therefore call this upper series of plates "side-covering plates." There are often slight interspaces between them throughout most of their depth. An examination of the series of photographs as also the wax models show that no pores are present leading into the interior of the test. These plates were on an average 13 mm. in thickness, the plates covering the mouth are merely enlarged side covering plates. They occupy the angles of those inter-radii which border the mouth region. These inter-radii are not five in number but three, namely those between II and III, III and IV, IV and V. This is because a secondary triradiate symmetry has been imposed upon the primitive pentamerous symmetry of this genus, *vide infra*.



TEXT FIGS. 9, 10, 11, 12.—Progressive views of reconstructed wax model of *Lepidodiscus* (*Agelacrinus*) *pileus*; *I*, *II*, *III*, *IV*, *V* = ambulacra; *s.cp.*, side-covering plates; *m.ai.*, mouth plate of anal inter-radius; *m.cp.*, mouth corner plate; *f.p.*, flooring plates. *By error in the figures, the ambulacra have been numbered V, I, II, III, IV instead of I, II, III, IV, V.*

FIG. 9.—Outermost view.

Two of the mouth-covering plates are of equal size. They are smaller than the third, which occupies the angle of the anal inter-radius.

The ambulacral groove is floored by a series of single oblong plates, which stretch across the groove, and show no trace of median suture or pore, figs. 10, 11. They do not correspond in number to the side covering plates, but are somewhat larger, figs. 10, 11. Jaekel (8, p. 17) has the same observation with regard to the flooring plates of Hemicystis. "Deren Zahl nicht immer genau so gross ist wie die Zahl der Saumplättchen, so dass wohl bisweilen je 2 auf einer solchen Subambulacral-Platte aufsitzen." I can find no correspondence in number between the side-covering and the flooring plates. At times, two side covering plates appear to rest on one flooring plate on one side of the groove, figs. 10, 11, but, on the other side, the corresponding plates lie on portions of more than one flooring plate. This may be due, however, to secondary distortion.

The above account of the structure of the ambulacral groove is confirmed by a study of a specimen of *Agelacrinus cincinnatiensis*, in which the side-covering plates have been dissolved away along most of the ambulacra. The flooring plates, which agree precisely with those of *A. pileus*, have been thus exposed. They show grooves along their border, which are the articulation of the upper series, Plate 1, fig. 2.

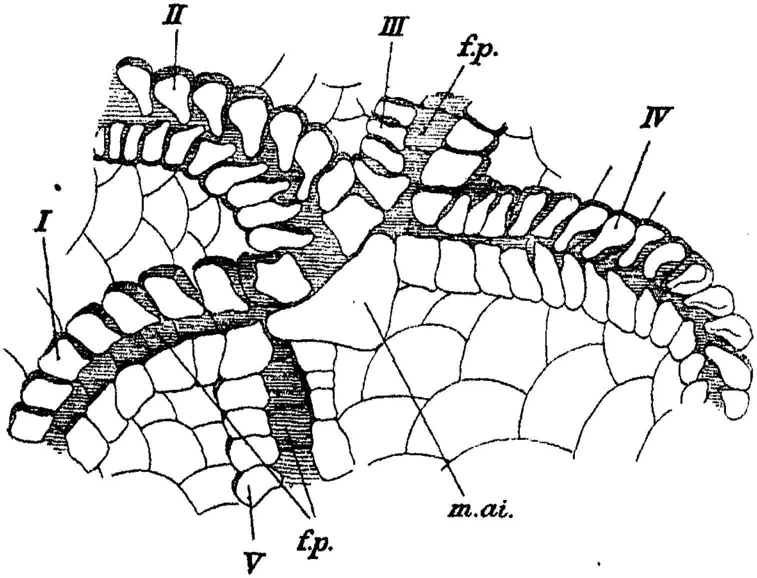


FIG. 10.—View $\frac{1}{4}$ mm. removed or 20 sections $\frac{1}{80}$ mm. thick.

The flooring plates enclose the mouth, except in the anal inter-radius. In the ground specimen of *A. pileus* they have been slightly displaced. They are more naturally preserved in the *A. cincinnatiensis* examined, Plate 1, fig. 2. The fact that the flooring plates do not enclose the mouth in the anal inter-radius is a necessary consequence of enlargement of this inter-radius. The plates of the mouth are merely the flooring plates of the ambulacra. The ambulacra I and V do not meet in the angle of the anal inter-radius, and consequently the mouth ring cannot be completed by these plates. The enlargement of the anal inter-radius has also produced the secondary fusion of radii I and II, and IV and V, a phenomenon not confined to Agelacrinus, but one found commonly in the Pelmatozoa. Jaekel (8, p. 8) has called attention to this, "Diese Verschiebung der Gabelung zwei Strahlen findet aber überall bei Pelmatozoen im analen Inter-radius statt, wo sich die Primärporen, das Parietalseptum und der After zwischen zwei Strahlen einschieben. Dadurch wird die Abgliederungsstelle der Radien I und V etwas nach den Seiten verschoben." The calcification of the plates must be secondary to the location of the internal organs, for these are formed first during ontogeny. Secondary symmetries in the ambulacral plates are thus readily accounted for.

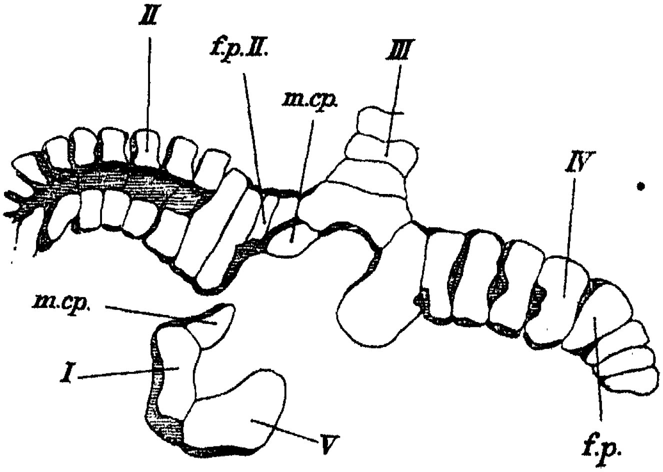


FIG. 11.—View 1 mm. removed or 40 sections $\frac{1}{40}$ mm. thick.

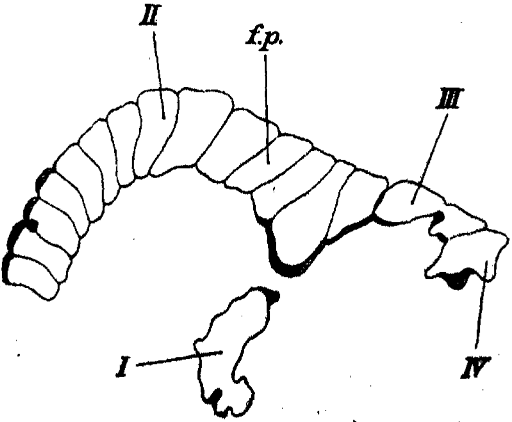


FIG. 12.—View $1\frac{1}{2}$ mm. removed or 60 sections $\frac{1}{40}$ mm. thick.

The mouth ring is further strengthened by plates, which underly the mouth-covering plates. These occupy the angles between II and III and III and IV. The third, which underlies the large mouth-covering plate of the anal inter-radius, completes the mouth ring in this region. It has been somewhat attacked by solution in both cases examined. The flooring plates of the mouth ring are thicker than those of the remainder of the ambulacra. No trace of any plates are to be observed underneath them. This would seem to indicate that the central part of the ventral region of Agelacrinus was occupied by a membrane with calcification weakly, or not at all developed. A similar appearance has been described in Edrioaster by Forbes and Bather. Bather has supposed that by the pulling in of this membrane a vacuum would be produced, thus fixing the animal to the sea floor.

No trace of any Madreporite was observed in Agelacrinus. Jaekel demands the absence of this organ throughout the Edrioasteroidea. Bather has, on the contrary, interpreted a structure on the thecal plate near the mouth in the anal inter-radius of Edrioaster as a Madreporite.

Theoretical Conclusions.—We have seen that there are two distinct views as to the structure of the ambulacrum in the Edrioasteroidea.

1. That which has found its latest supporter in Jaekel asserts that the ambulacral groove possesses single flooring plates. No openings are present between these, or, if they were present, they served as genital orifices.

2. That which is advocated by Dr. Bather, founded upon a study of Edrioaster. This states that there was a double series of alternate flooring plates. Between these were openings, through which passed ampullæ.

The results of the above investigation shows that Jaekel is correct with respect to the structure of the ambulacral groove in the Agelacrinidæ. There appears no reasonable doubt, however, that Edrioaster possesses a double series of alternating flooring plates, and between these plates are pores. Dr. Bather has been kind enough to show me an exceptionally well-preserved specimen of *Edrioaster Bigsbyi*, which leaves no doubt upon this point. Dr. Bather's view that through these pores protruded either podia or ampullæ, is, however, open to criticism. The pores are at the extremity of a groove, in such a position that they lie immediately under the hinge of the covering plates. The groove which leads to the pore opens out gradually, and suggests that it served to carry water to the pore, which would then have a respiratory function. That some members of the Edrioasteroidea should show respiratory pores, whilst others do not, is in accordance with the structure of the group as a whole. Jaekel divides the Edrioasteroidea into two sub-groups. The Thecocystideæ, including Edrioaster; and the Agelacrinidæ. The former are characterised by their firm skeletons, the latter by their imbricating plates. The forms with firm skeletons would require respiratory pores. The Agelacrinoidea would, on the contrary, present large surfaces of membrane to the surrounding sea-water when they were not in the state of collapse in which they are generally found.

There is very strong evidence that no member of the group, primitive as it is, lay in a direct ancestral line between Pelmatozoa and Eleutherozoa, as advocated by Hæckel and Bather. No Edrioasteroid is known which does not possess both covering and flooring plates. The Asteroids, which lay at the base of the Echinoid stem, as we shall now seek to show, possess only a single series of ambulacral plates. The assertion of the presence of a double series in the embryo is without foundation. It is impossible to suppose that the complicated ambulacrum and firm skeleton of Edrioaster gave birth to the primitive simple ambulacrum and movable skeleton of the Asteroids. With regard to the relationships between the Asteroids and Echinoids, Johannes Müller remarked in 1853: "Die Vergleichung eines Seeigel und eines Seesternes war immer ein anziehender Punkt für die Speculation." In this same paper, Müller (15, p. 170) draws comparisons which have since become classical. "Stellen wir uns vor, die Ambulacralplatten des Echinus weichen auseinander, und werden durch Haut vereinigt, umwachsen aber das Ambulacralgefäss und den Nerven von unten, so erhalten wir aus dem Echinus die Asterie; stellen wir uns eine Asterie vor, bei welcher die häutigen Gebilde über die Nerven und Gefässe von den Ambulacralplatten aus ossificiren, und lassen wir die Nath der wirbelartigen Fortsätze unter den Gefässen weit klaffen, so erhalten wir aus der Asterie die Verhältnisse der Echinen. Ein dritter Fall wäre, dass die Ambulacral-platten zugleich die Vereinigung der Echinen über dem Nerve und Gefäss erzielen, als die Fortsätze der Asterien entwickeln. Dieses kommt in der That bei Cidaris am vorderen Theil der Ambulacra vor, wo die Ambulacral-platten an der innern Seite der Porenreihen Fortsätze senkrecht nach innen gegen die Höhle der Schale abschicken, welche von beiden Seiten die Stämme der Ambulacralgebilde zwischen sich nehmen."

"Ausser Cidaris hat auch Clypeaster rosaceus und altus oder überhaupt die Gattung Echinanthus denjenigen Theil der Ambulacralplatten, welcher den vertebralen Fortsätzen der Asteriden analog ist, in der innern Tafel ihrer Ambulacral-platten. Hier nehmen alle Ambulacral-platten daran Theil und es tritt sogar die Vereinigung von rechts und links durch Nath ein. Dieser Ambulacralboden liegt, wie bei den Asteriden, unter den Stämmen der Ambulacralgefässe und Nerven. Dagegen ist die äussere Tafel der Ambulacral-platten über dem Nerven- und Gefässtamme analog der häutigen Bedeckung der Ambulacra der Asteriden. Damit ist nunmehr sattsam bewiesen, dass in der That der Bau der Ambulacra in den Echiniden und Asteriden gänzlich abweicht und dürfen Cidaris und Echinanthus als der Schlüssel zum Verständniss dieser Abweichungen angesehen werden."

The justice of these observations is strikingly illustrated by the discovery of the double series of plates in Palæodiscus. The lower series of ambulacral plates in Palæodiscus must be regarded, just as the auricles of Echinus and the ambulacral processes of Cidaris, as the representatives of the ambulacral plates of the Asteroids.

Lovén (11, p. 38) has shown "that the auricles of the Ectobranchiates are seen to adhere to the ambulacra as distinct and independent parts joined mainly to them by means of articulation, and to increase by their own growth, both surfaces, the auricular and the ambulacral, during the constant fluctuations of absorption and renewal mutually maintaining their firm connection."

This statement shows that embryology justified the homologies drawn above, and that we have in the embryo two distinct series of plates, the outer of which are the true Echinoid plates, the inner which become auricles are the Asteroid ambulacrals.

Semon and Lang have suggested that the true Echinoid plates may be derived by the overgrowth of the adambulacral plates of Asteroids, a view which would support this theory.

We must conclude, therefore, that whilst a double series of plates, namely, an outer series peculiar to the Echinoid, perhaps derived from the adambulacrals of Asteroids, and an inner series homologous with the plates of an Asteroid occur in the ambulacrum of all the Echinoids, a complete double series occurs in Palæodiscus, which is therefore entitled to be placed at the base of the Echinoid stem. It is not alone in the structure of the ambulacra that Palæodiscus shows itself to be the most primitive of Echinoids, for we have seen that the interambulacral areas present many ideally primitive Echinoid structures.

That the transition must have been from Asteroid to Echinoid and not *vice versâ*, the possession of a lantern of Aristotle by the latter forms is quite sufficient proof.

MacBride (12, p. 316) in a recent paper has adduced embryological evidence to derive the Echinoids from the Asteroids; he shows: "That in the just metamorphosed sea urchin the humped dorsal surface is greater in extent than the flat ventral one, and the radial canals extend straight outwards from the water vascular ring and end in prominent terminal tentacles, both of which are Asteroid features." MacBride also remarks upon the "highly developed Pedicellariæ amongst the Echinoidea." Amongst Asteroidea they are by no means universal, and numerous transitional forms are found showing their origin from the spines; in a word, pedicellariæ have been developed amongst the Asteroidea and inherited ready-made, so to speak, by the Echinoidea.

As to the Pelmatozoan ancestor of the Eleutherozoa it is better to leave that in the realms of controversy, Asteroids are known from the Cambrian period, and it is very probable that this ancestor was pre-Cambrian.

LITERATURE.

1. Bather. 1898–99. "Studies in Edrioasteroidea." 'Geol. Mag.,' N.S., dec. IV, vol. 5, 6.
   1901. "What is an Echinoderm?" 'J. London Coll. Soc.,' vol. 8.
   1900. "A Treatise on Zoology, Part III, The Echinoderma."
2. Billings, E. 1858. ("On the Cystideæ of the Lower Silurian Rocks of Canada.") 'Canadian Organic Remains,' dec. III, pp. 9, 74.
3. Forbes, E. 1848. ("On the Cystideæ of the Silurian Rocks of the British Islands.") 'Mem. Geol. Surv., Great Brit.,' vol. 2, Part 2.
4. Giesbrecht, W. 1880. "Der feinere Bau der Seeigelzähne." 'Morph. Jahrbuch,' vol. 6.
5. Gregory. 1897. "On Echinocystis and Palæodiscus." 'Quart. Jour. Geol. Soc.,' vol. 53, pp. 123–136.
6. Hæckel. 1896, "Die Amphorideen und Cystoideen, etc." 'Festschr. für Gegenbaur,' No. 1.
7. Hall. 1847, 1852, 1859. 'Palæontology of New York, vol. 1, 2, 3, in Natural History of New York.'
   1858. 'Report on the Geological Survey of the State of Iowa, vol. 1, Part II, Palæontology.'
8. Jaekel, O. 1899. 'Stammesgeschichte der Pelmatozoen,' vol. 1.
9. Jackson, R. T. 1896. "Studies of Palæechinoidea." 'Bull. Geol. Soc. Amer.,' vol. 7, pp. 171, 246.
10. Lang. 1896. 'Text Book of Comp. Anat.,' English Translation, vol. 2, p. 355.
11. Lovén. 1892. 'Echinologica Bihang. Svensk. Vet. Akad. Hand.,' vol. 18, Afd. IV, No. 1.
12. MacBride. 1903. "The Development of Echinus Esculentus." 'Phil. Trans.,' Series B, vol. 195, pp. 285—327.
13. Meek, F. B. 1873. 'Ohio Pal.,' vol. 2.
14. Miller and Faber. 1892—93. 'Cincin. Soc. Nat. Hist. Journ.,' vol. 15.
15. Müller, Joh. 1854. "Ueber den Bau der Echinodermen." 'Abhand. d. Kgl. Akad. d. Wissensch., Berlin.'
16. Neumayr, M. 1881. "Morphologische Studien über fossile Echinodermen." 'Sitz. Ber. d.k.k. Akad. d. Wiss. in Wien,' vol. 84.
    1889. 'Die Stämme des Thierreiches,' vol. 1.
17. Roemer. 1851. "Beiträge zur Kenntniss der Fossilen Fauna des Devonischen Gebirges am Rhein." 'Verh. d. Natur. Hist. Ver. f. Rheinlande und Westfalen,' vol. 8, p. 372.
18. Salter. 1857. ("On some New Palæozoic Starfishes.") 'Ann. Mag. Nat. Hist.,' Ser. 2, vol. 20.
19. Schmidt, F. B. von. 1874. "Ueber einige neue und wenig bekannte Baltisch-Silurische Petrefacten." 'Mem. Acad. Imp. Sci.,' St. Petersburg (7), vol. 21, pp. 34 and 35.
20. Sollas, W. J. 1889. "On Silurian Echinoidea and Ophiuroidea." 'Quart. Journ. Geol. Soc.,' vol. 45, 1889, pp. 692—716.
    1903. 'Phil. Trans.,' Series B, vol. 196.
21. Sowerby, G. B. 'Zoological Journal,' vol. 2.
22. Thomson, C. Wyville. 1861. ("On a new Palæozoic Group of Echinodermata.") 'Edin. New Phil. Journ.,' N.S., vol. 13, pp. 106—117.
23. Wright. "British Fossil Echinodermata of the Oolitic Formations," vol. 2; "The Asteroidea and Ophiuroidea." 'Palæontogr. Soc.,' 1863—1880.
24. Zittel, K. A. 1879. 'Handbuch der Palæontologie, 1. Band, Palæozoologie.'

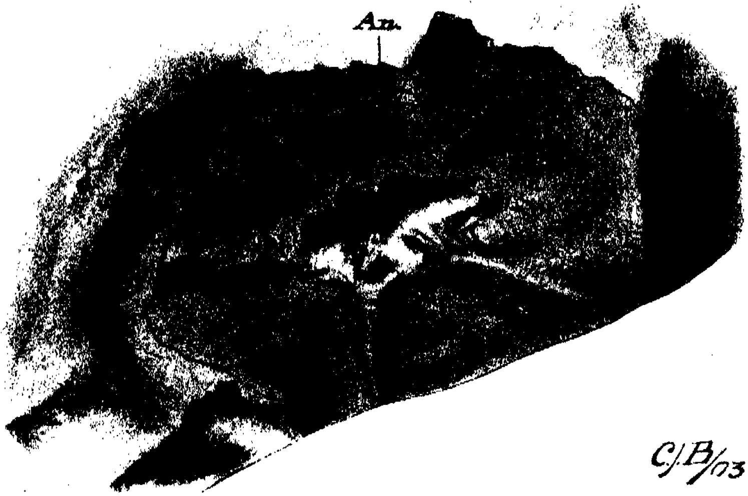


FIG. 1.—Cast of *Palæodiscus ferox* in the Oxford Museum; *An* = Anus.

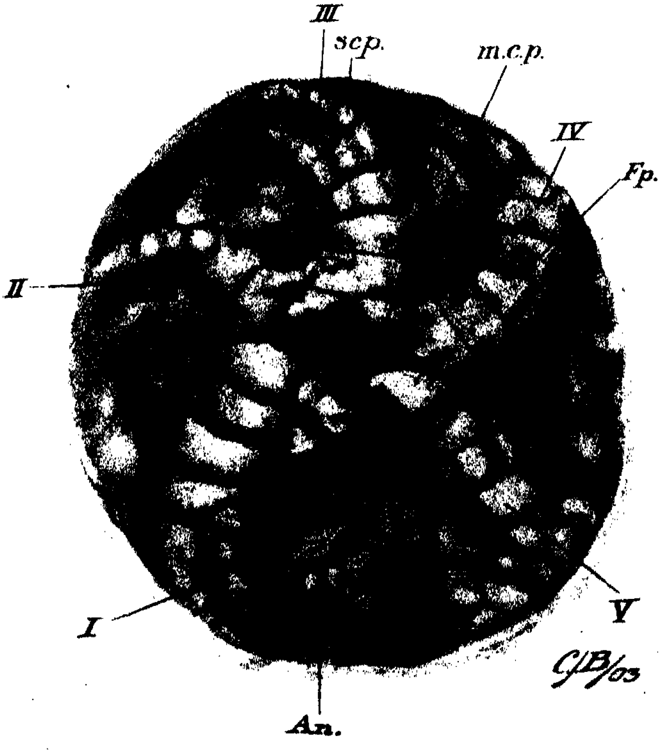


FIG. 2.—Upper view of *Agelacrinus cincinnatiensis* in the Oxford Museum: *I, II, III, IV, V,* are Ambulacra; *An* = Anus; *F.p.*, flooring plates; *s.c.p.*, side covering plates; *m.c.p.*, mouth corner plate.

"On the Action of Radium Emanations on Diamond." By Sir WILLIAM CROOKES, F.R.S. Received June 9,—Read June 16, 1904.

When diamonds are exposed to the impact of radiant matter in a high vacuum they phosphoresce of different hues, and assume a dark colour, becoming almost black when the bombardment is long continued.[*]

Some diamonds blacken in the course of a few minutes, while others require an hour or more to discolour.[†] This blackening is only superficial, and although no ordinary means of cleaning will remove the discoloration, it goes at once when the stone is polished with diamond powder. The fact that the black stain is not affected by ordinary oxidising reagents would seem to show that it is not due to a layer of amorphous carbon; but it might be graphite, which is much more resistant to oxidation. Becquerel has shown that graphite is converted into graphitic oxide by long digestion in a warm mixture of potassium chlorate and strong nitric acid, while diamond—even in a very finely powdered state—is absolutely unaffected by the mixture.[‡]

Some forms of graphite dissolve in strong nitric acid; others require a mixture of highly concentrated nitric and potassium chlorate to dissolve them, and even with this intense oxidising agent some graphites resist longer than others. M. Moissan has shown that the power of resistance to nitric acid and potassium chlorate is in proportion to the temperature at which the graphite has been formed, and with reasonable certainty we can estimate this temperature by the resistance of the graphite to this reagent.

Judging from the long time required to remove the superficial darkening from diamond, the graphite is as resistant as that formed at the temperature of the electric arc.

On one occasion when I had blackened the surfaces of diamonds by molecular bombardment *in vacuo* M. Moissan was present, and took some away with him for further examination. He subsequently reported the results in the '*Comptes Rendus*.'[§] He heated the diamond to 60° in an oxidising mixture of potassium chlorate and fuming nitric acid prepared from mono-hydrated sulphuric acid and potassium nitrate fused and quite free from moisture. The action on the black layer is very slow. There is produced graphitic oxide, which at an increased temperature yields pyrographitic acid, easily destroyed by nitric acid. Hence the variety of carbon which coated the diamond was graphite. The transformation of diamond into graphite requires the high temperature of the electric arc. The higher the temperature to which graphite is raised the greater is its resistance to oxidation. M. Moissan concludes that the temperature reached by the surface of the diamond in my radiant matter tubes is probably about 3600°.

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[*] 'Phil. Trans.,' 1879, Part II, p. 658, par. 625.

[†] At a lecture before the Royal Institution on June 11, 1897, I exposed a flat macle crystal of diamond to radiant matter bombardment before the audience for about 5 minutes, a strip of metal covering part of the stone. On removing the diamond from the vacuum tube and projecting its image on the screen with the electric lantern, the image of the darkening was very apparent.

[‡] 'Ann. de Chim. et de Phys.,' [4], vol. 19, p. 392.

[§] Vol. 124, No. 18.

The β-rays from radium having like properties to the cathode stream in a radiant matter tube, it was of interest to ascertain if they would exert a like difference on diamond. Two Bingara diamonds, A and B, weighing respectively 0·960 and 1·020 grains, were selected as near as the eye could judge of the same size and colour—very pale yellow, technically known as "off colour." Diamond A was put in a drawer far removed from radium or any radio-active body. Diamond B was kept close to a quartz tube containing about 15 milligrammes of pure radium bromide sealed *in vacuo*. It phosphoresced brightly and continued to glow the whole time of the experiment.

After a fortnight the two diamonds were put side by side and compared. I could see no appreciable difference in colour between them. Diamond B was now replaced close to the quartz tube of radium, and they were kept in contact for six weeks. At the end of that time examination again showed scarcely any difference between the two. The one which had been near the radium might be a little the darker of the two, but the difference was too slight to enable me to speak positively.

Diamond B was now put inside a tube with radium bromide, the salt touching it on all sides, as it was thought possible that a screen of quartz might interfere with the passage of emanations which would act on the diamond. The comparison diamond was kept removed from the emanations as before. The experiment was continued for 78 days, when the two diamonds were again examined. There was now a decided difference in colour between them; diamond A was of its original pale yellow "off colour," and diamond B was of a darker appearance and of a bluish-green tint, with no yellow colour apparent.

It thus appears that the property which radium emanations possess of darkening transparent bodies which they impinge upon—a property very marked in the case of glass, and less with quartz—also holds good in the case of diamond.

Diamond B was now heated to 50° C. in a mixture of strongest nitric acid and potassium chlorate for 10 days, the mixture being renewed each day. At the end of this time the diamond had lost its dull surface colour, and was as bright and transparent as the other stone, but its tint had changed from yellow to a pale blue-green.

The radium emanations have therefore a double action on the diamond. The β-rays (electrons) effect a superficial darkening, converting the surface into graphite in a manner similar to, but less strongly than, the more intense electrons in the cathode stream. But the alteration of the body colour of the stone by emanations which are obstructed by the thinnest film of solid matter, even by a piece of thin paper, is not so easy to understand. A superficial action might be expected, but not one penetrating through the whole thickness of the diamond. I believe the alteration of colour is a secondary effect; in presence of radium the diamond is extremely phosphorescent, and it continues to shine during the whole time of the experiment. This constant state of vibration in which the diamond was kept for many weeks may have caused an internal change revealing itself in a change of colour. Indeed, it is not difficult to suppose that a chemical as well as a physical action may result. If the yellow colour is due to iron in the ferric state a reduction to the ferrous state would quite account for the change of colour to a pale blue-green.

This alteration of colour may be of commercial importance. If "off colour" stones can be lightened their value will increase, while if the prolonged action of radium is to communicate to them a decided colour they would be worth much more as "fancy" stones.

[*Added June* 16, 1904.—After the 10 days' heating in the above acid mixture the two diamonds were put together in a glass tube and carried about for 25 days, sometimes loose and sometimes in the tube. They then were laid near together on a sensitive film in total darkness for 24 hours. On developing, diamond B had impressed a strong image on the film, but only a very faint mark could be seen where the other diamond had been. Probably this slight action was due to a little radio-activity induced in A during its 25 days' proximity to B.

The experiment was then repeated for confirmation, allowing the diamonds to remain on the sensitive surface for only 5 hours. On development, a good image of diamond B was seen, but not so black as in the former case.

The fact that diamond B was strongly radio-active after it had been away from radium for 35 days, for 10 of which it was being heated in a mixture powerful enough to dissolve off its outer skin of graphite, seems to me proof that radio-activity is by no means a simple phenomenon. It not merely consists in the adhesion of electrons or emanations, given off by radium, to the surface of an adjacent body, but the property is one involving deep-seated layers below the surface, and like the alteration of tint is probably closely connected with the intense phosphorescence the stone had been experiencing during its 78 days' burial in radium bromide.]

"On a Direct Method of Measuring the Coefficient of Volume Elasticity of Metals."

By A. MALLOCK, F.R.S.

Received April 19,—Read June 2, 1904.

For most hard materials the coefficient of volume elasticity is usually calculated from measurements of Young's modulus or of the coefficient of rigidity, either of which, when Poisson's ratio is known, suffices for its determination. Although, however, the total alteration of volume for a given pressure can be calculated from the coefficient thus obtained, it is only for isotropic material that the alteration of dimensions in any given direction can be inferred from it.

The following direct method of measuring the coefficient of volume elasticity is of some interest, as it allows of the linear contraction or extension in any given direction, caused in a substance by fluid pressure, to be measured independently of other changes of form.

When a long circular cylinder is acted on by internal fluid pressure, if the walls are very thin compared to the diameter of the cylinder, the stress in the material parallel to the axis is just half the stress at right angles to the axis in the tangent plane. The conditions of strain and stress in the walls of the cylinder can be expressed in terms of the volume elasticity and rigidity of the material as follows:—

Consider a small cube of the material, with edges parallel to the axis (X), radius (Y), and tangent of circular section (Z) of the cylinder respectively. Let K be that part of the stress which produces alteration of volume, and N_{xz} and N_{yz} the parts which produce shear in the planes XZ and YZ.

The total force acting parallel to Y, *i.e.*, in the direction of the radius, vanishes in comparison with the forces at right angles to it when the walls of the cylinder are thin, for while the radial force is O at one surface of the cylinder, and equal per unit area to the fluid pressure (P) on the other, in the two directions at right angles to the radius the stress is of the order Pr/t ($= 2P'$), where r is the radius and t the thickness of the wall.

Hence we have the following relations between K, N, and P':

$$\begin{aligned} K + N_{xz} + N_{yz} &= 2P' \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1),\\ K - N_{xz} \qquad\quad &= P' \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2),\\ K \qquad\quad - N_{yz} &= O \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3), \end{aligned}$$

whence

$$K = P' \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4).$$

That is, the alteration in the length of a cylinder caused by fluid pressure depends solely on the coefficient of volume elasticity.*

Since K is that part of the applied force which goes to produce alteration of volume, we have, if κ be the coefficient of volume elasticity ($\kappa = \kappa_x + \kappa_y + \kappa_z$) and e_x, e_y, e_z, the alterations of dimensions caused in the cube by volume expansion in X, Y, Z,

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* It may be shown that this result is independent of the thickness of the walls of the circular cylindrical tube.

$$\kappa_x = \frac{P'}{e_x} = P\frac{r}{2te_x}.$$

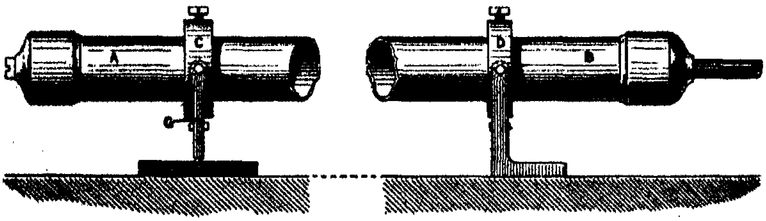
In isotropic materials $\kappa_x = \kappa_y = \kappa_z$ and $e_x = e_y = e_z$, so that

$$\kappa = Pr_2/6te.$$

The ease with which minute variations of length can be measured in the case of rods or tubes allows of a very accurate determination of that component of K which refers to stress parallel to the axis of the tube. For this purpose it is merely necessary to so mount a suitable length of tube of the material to be experimented on that it can be subjected to strain by internal fluid pressure, and the variation of length caused by that pressure be observed.

I have used this method with steel, copper, and brass tubes in order to see whether *annealing* altered the value of κ. The arrangement employed is shown in fig. (1).

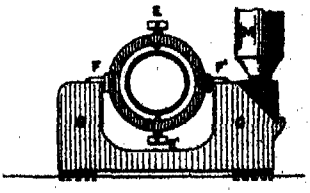
FIG. 1.



The tube AB is closed by caps at each end. Through the cap at B a small pipe connected with a pressure pump and gauge is introduced. The cap at A has a small hole in it, which can be closed with a plug after the tube has been filled with water.

The tube is embraced at C and D by gymbal rings fig. (2) where the steel points EE′ are closed on the tube, and the pivots FF′ rest at (D), fig. (1) on a fixed support, and at C, fig. (1) on a rocking support G. This rocking support carries a small reflecting prism H, whose upper surface is parallel to the axis of the tube, and passes through the axis FF′ of the gymbal ring. The movement of a mark on this surface of the prism was measured by the microscope M, fig. (2) a ⅛-inch objective being used.

FIG. 2.



The only practical difficulty met with was the variation of temperature of the room during the experiments. From this cause it was generally found that the zero was slowly altering, but the temperature effect can be readily eliminated from the observations.

In the experiments, the results of which are recorded below, the maximum fluid pressure in the tube was 400 lbs. per square inch. The longitudinal extension was measured at 100, 200, 300, and 400 lbs. pressure, and the extensions when corrected for temperature and plotted in terms of pressure lay on a straight line within the limits of error.

Table of Results.

Condition.	Length between supports in inches.	Outside diam. in inches.	Thickness of wall in inches.	Total extension at 400 lbs. per square inch.	$3\kappa_x$ in C.G.S. units.	κ from experiments.*
Seamless Steel Tube.						
Hard	60	0·75	0·0190	$2·8 \times 10^{-3}$	$18·4 \times 10^{11}$	$18·41 \times 10^{11}$
Annealed				2·75 „	18·2 „	
Solid Drawn Brass Tube.						
Hard	50	0·415	0·0185	$2·12 \times 10^{-3}$	1105×10^{11}	Different samples from $10·85 \times 10^{11}$ to 10·02
Annealed				2·09 „	1075 „	
Solid Drawn Copper Tube.						
Hard	50	0·4485	0·0382	$5·62 \times 10^{-4}$	23×10^{11}	$16·84 \times 10^{11}$
Annealed				7·1 „	16·2 „	

* From Everett's "C.G.S. System of Units."

The value of $3\kappa_x$ is given in the table to facilitate comparison with other measures, as $3\kappa_x$ is the value κ would have if the material had the same properties in all directions as it has in that of the axis of the tube.

The case of copper is remarkable, for in its hard drawn state it extends less in the direction of the drawing than a similar tube of steel would when equally strained.

"On the Relation between the Spectra of Sunspots and Stars."

By Sir NORMAN LOCKYER, K.C.B., LL.D., F.R.S.

Received June 8,—Read June 16, 1904.

As the period throughout which the observations of widened lines have been made at South Kensington now includes two maxima and three minima epochs of solar activity, it has seemed desirable to discuss the results obtained, taking into account the chemical origins of the lines affected in passing from the photosphere to the sunspot nuclei. This is going on, but in anticipation of its publication, I desire to direct attention to one of the conclusions arrived at in its bearing upon the question of the temperature conditions of the Arcturian and lower type stars, which formed part of the subject of a recent paper.[*]

Since 1894, when the last discussion of the widened line results was published,[†] nearly 10,500 observations of lines in sunspot spectra have been made at South Kensington. An analysis of these lines, in respect to their origins, shows that *the elements chiefly affected during the period* 1892—1903, *inclusive, were Vanadium and Titanium.*

The great importance of Vanadium and Titanium in sunspot spectra has also been demonstrated by Father Cortie during his observations in the B—D region at Stonyhurst.[‡]

It was foreshadowed in a previous paper on the chemical classification of the stars[§] that it seemed probable that, as the result of further work, the "genera" then proposed might have to be split up into "species." During the more recent research mentioned above the temperature classification was tested by comparing the relative intensities of the red and ultra-violet ends of the spectra of stars, situated on various horizons of the temperature curve, including Capella and Arcturus, which, according to the original general classification, belong to the same type, viz., "Arcturian." It was found that the spectrum of Capella extended on an average about 70 tenth-metres further into the ultra-violet than that of Arcturus, whilst the red portion of the spectrum is certainly stronger in the latter. That is to say, *the general temperature of Arcturus is probably appreciably lower than that of Capella.*

The next step was to see if chemical change accompanied this reduction of temperature, and if so, whether the change was in any way related to the change from the photosphere to the sunspot spectrum.

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[*] 'Roy. Soc. Proc.,' vol. 73, pp. 227—238, 1904.

[†] 'Roy. Soc. Proc.,' vol. 57, p. 199, 1894.

[‡] 'Monthly Notices (R.A.S.),' vol. 63, No. 8, pp. 479—480, June, 1903.

[§] 'Roy. Soc. Proc.,' vol. 65, p. 191, 1899.

In comparing, for this purpose, the spectra taken with the 6-inch Henry prismatic camera it was noticed that certain lines were relatively intensified in passing from the spectrum of Capella to that of Arcturus.

Similar comparisons of the Fraunhoferic spectrum with the spectra of Capella and Arcturus respectively were next made. This work led to the following conclusions :—(1) That the line absorptions of Capella and the sun are practically identical; (2) that although, speaking generally, the same lines occur in the spectra of the sun and Arcturus, yet in the latter many lines are relatively more intense than in the former. Moreover, in the great majority of such cases *the lines so intensified are probably due to Vanadium and Titanium.*

Thus we see that whilst the temperature classification mentioned above certainly places Arcturus on a lower temperature level than Capella and, therefore, the sun, the evidence obtained from a study of the line absorptions of Arcturus and of sunspots indicates very clearly that the temperature of the Arcturian absorbing atmosphere is about the same as that of the sunspot nuclei during the above-mentioned period.

This conclusion justifies the ideas formulated by De la Rue, Stewart, and Loewy that the spots are produced by the downrush of cooler material.

In a recent publication,* which has been received here since the above-mentioned comparisons were completed, Professor Hale suggests that because the lines which are widened in sunspots appear as strong dark lines in Piscian stars, the effect may be produced because sunspots are more numerous in such stars. From the evidence adduced above it seems a far more probable explanation to suppose that these lines are intensified in sunspots, and strengthened in those stars which have been placed on lower temperature levels than the sun, because the general temperature conditions are similar. That is to say, the fall of temperature experienced by the metallic vapours in passing from the photosphere to the spot nucleus is of the same order as that to which an absorbing atmosphere is subjected in passing from the temperature conditions of Capella or the sun to that of Arcturus or the lower temperature stars.

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* "The Spectra of Stars of Secchi's Fourth Type" ('The Decennial Publications,' Chicago University, 1903).

"On the Physical Relation of Chloroform to Blood." By A. D. Waller, M.D., F.R.S. Received May 5,—Read June 9, 1904.

In connection with the preliminary communication by Moore and Roaf on certain physical and chemical properties of solutions of chloroform in water, saline, serum, and hæmoglobin,[*] it may be of interest to publish the following communication. The close similarity of the conclusions arrived at independently by different observers is such as to render the two communications mutually corroborative, and although the present communication forms part of a report by A. D. Waller and J. H. Wells, which is technically the property of a Special Chloroform Committee of the British Medical Association, there is obviously no reason why it should be withheld from publication. It was originally presented as long ago as June 19, 1903, and I have since that time extended the experimental data upon which the conclusion rests. In order, however, to preserve the complete independence of the two contributions I have preferred to communicate it in its original, and perhaps imperfect, form. The importance of the blood as a chloroform carrier, by reason, presumably, of an easily dissociable compound, is the conclusion of principal importance arrived at in both series of investigations.

The original text of the report is as follows :—

"Our attempts to recover a known weight of chloroform from blood, by the French method (extraction *in vacuo* followed by digestion with alcoholic potash and titration of chlorides), led us to make two simple experiments that very strikingly illustrate the fundamental difference between blood and simple salt solution or water as regards their absorptive power towards chloroform vapour. The first of these experiments shows that equal volumes of blood and of normal saline are capable of absorbing very different volumes of chloroform vapour. The second shows the converse fact that very different volumes of chloroform vapour are obtainable by evacuating equal volumes of blood and of water, or of normal saline. In the first experiment the absorption by blood is greater than that by water. In the second experiment the delivery from blood is less than that from water. The inference from these two data is that blood possesses greater affinity for chloroform than does water, and that, therefore, in the transfer of chloroform by blood from the pulmonary air to the nervous centres that fluid does not act as a simple solvent, but rather as a temporary retaining and restraining medium, that helps to convert irregular into constant flow. The blood has thus a controlling effect upon the process of anæsthesia that may be compared to the action of a flywheel, or to that of the arterial elasticity, by which intermittent force effects constant flow. The blood acts as a chloroform reservoir (or as an ether reservoir if ether be the anæsthetic employed).

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[*] Communicated by Professor Sherrington, received April 12, read May 5, 1904. [*Ante*, pp. 382—412.]

In the *first experiment* we compared manometrically the absorptive power of blood and of water by introducing a known volume of each liquid in the two identical closed flasks connected with two petroleum manometers, and previously filled with chloroform and air of identical percentage.

The figures of a first trial were as follows for 50 c.c. of blood* and of water respectively in flasks of 600 c.c. capacity filled with chloroform vapour at 17 per cent. :—

Time of absorption.	Flask A. Water-absorption pressure.	Flask B. Blood-absorption pressure.
1 min.	186 mm.	248 mm.
20 mins.	191	246
60	192	246

A second trial, with the blood and water transposed, and the flasks charged by chloroform and air at lower $CHCl_3$ percentages gave :—

$CHCl_3$ in flask.	Time of absorption.	Flask A. Blood-absorption pressure.	Flask B. Water-absorption pressure.
10 per cent.	4 mins.	110 mm.	56 mm.
	7	140	82
	12	156	88
	16	167	90
	21	170·5	92
6 "	0	35	34
	4	62·5	43
	9	69	44
	13	71	45
	17	72	50
	60	75	54

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* The blood in this experiment was taken from the chloroformed animal, *i.e.*, contained *some* chloroform. Blood fully saturated with chloroform has no further absorptive power. Blood from an unchloroformed animal has a maximum absorptive power. We have made preliminary trials to learn whether a rapid method of estimating the degree of saturation of blood with chloroform can be based on this principle, but our results at present are not sufficiently advanced for report. The figures given in the text are preliminary approximations, obtained by a first trial of a method which will require much further elaboration as regards its apparatus. It will be noticed that the gross difference in favour of blood comes out in spite of the fact that the water value and solvent power of blood are about 0·8 that of water.

The first part of the absorption is lost in each case during introduction of fluid into the bottles. The first pair of readings are taken at the end of the second minute. The second readings at the end of the fourth minute, when both bottles are equally shaken for half a minute, after which the third readings are taken. The fourth and fifth readings are similarly taken at the seventh minute, the bottles being shaken a second time, S_2.

The bottles are left at rest for 7 minutes before the last readings, which show that the absorption has been nearly but not quite completed.

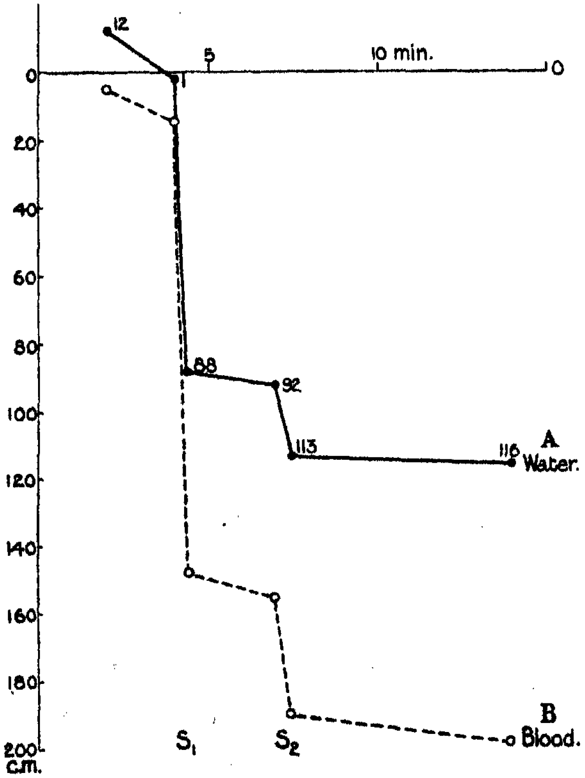

Figure showing Absorption Curves of Chloroform Vapour by Water and by Blood.

The vapour in the two bottles was then passed into and through two densimeter bulbs by water displacement. The increments of weight in the two cases were: in A 0·054 gramme, in B 0·032 gramme, showing that the residual atmosphere in A (water) contained more chloroform vapour than that in B (blood).

In the *second experiment* the apparatus consisted of (1) a distilling flask (containing the fluid to be evacuated, and a known weight of chloroform in a small glass bulb), (2) a receiver, and (3) a Geryk air-pump.

The receiver is first evacuated while shut off from the distiller. It is then shut off from the pump, and placed in connection with the distilling flask, with the result that the liquid in the latter boils and gives up its dissolved gases, which are for the most part drawn over into the receiver.

The evacuation of $CHCl_3$ is completed (in the case of saline; it is not completed in the case of blood) by gentle heat, and by opening the inlet of the distilling flask so that a rush of air takes place through the distiller to the receiver. The inlet tube is drawn out to a fine point, and reaches to the bottom of the distilling flask; the outlet tube is provided with a froth-bulb. Finally the quantity of $CHCl_3$ in the receiver is estimated by Harcourt's method.

In a *first trial* of this experiment with water in the distilling flask the result was as follows:—

Weight of $CHCl_3$ taken	0·082 gramme
„ recovered.........	0·065 „
Deficit.....................	0·017 „ or 21 per 100.

This considerable deficit was attributable to an insufficient capacity of the receiver as compared with that of the distiller and froth-bulb. That this was the case is shown by the figures of a second trial, in which a larger receiver was taken (of 1332 c.c. capacity in place of 400 c.c. capacity in the previous trial).

In this *second trial* the figures came out:—

Weight of $CHCl_3$ taken	0·112 gramme
„ recovered.........	0·109 „
Deficit.....................	0·003 „ or 3 per 100.

The similar experiment, with blood in place of water, gave a very different result, the deficit of evacuation being much greater, and clearly signifying that the chloroform is not merely in solution, but held in combination. In a carefully conducted trial made with 50 c.c. of whipped bullock's blood, to which 0·108 gramme of $CHCl_3$ had been added, the weight recovered was only 0·014 gramme; *i.e.*, the deficit was 0·092 gramme, or 85 per cent. It is evident, therefrom, that the absorption of chloroform by blood does not follow Henry's law.

This conclusion is in agreement with that arrived at by previous observers, Hermann, Schmiedeberg and others, to the effect that chloroform combines with the lecithin of blood. It is also in harmony with the modern theory of anæsthesia as presented by recent writers (H. Mayer, Overton, H. Meyer)* to the effect that the action of anæsthetics upon the several tissues and fluids of the body depends upon a "coefficient of partage, in which the affinity between anæsthetic and fatty matter is the principally effective factor."

From the foregoing observations (which should properly have been published by the Special Chloroform Committee in July of last year) it is clear that the conclusions are substantially identical with that arrived at by Moore and Roaf, viz., that the absorption of chloroform vapour is greater by blood than by saline, and that blood acts as chloroform carrier to the tissues just as it acts as oxygen carrier. It is a minor point of difference between the two independently presented conclusions, that whereas Moore and Roaf find no proof of any special combination between chloroform and "lipoids" as previously urged by German observers, we have in the report of our experiments admitted that the combination which certainly takes place between chloroform and protoplasm may possibly be accounted for on the lipoid theory.

But the question whether chloroform can combine with all protoplasm indifferently, or with its fatty constituents (lecithin, cholesterin) more particularly is a subsidiary issue, in respect of which neither the observations of Moore and Roaf, nor our own, contain any decisive evidence. On the one hand we are in presence of the fact that all protoplasm is subject to the influence of chloroform, on the other with the fact that all protoplasm is associated with fatty constituents of which lecithin is the most universal representative. Lecithin is widely distributed in vegetable as well as in animal protoplasm; it is present in blood-serum, which, as shown by Moore and Roaf, has a solvent power towards chloroform not far short of that possessed by blood.

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* Schmiedeberg, '*Grundriss der Pharmakologie*'; *Overton*, '*Pflüger's Archiv*'; H. Meyer, 'Arch. f. exp. Path. u. Pharm., vol. 42, p. 109, 1899; Höber, 'Physikalische Chemie'; Gottlieb, 'Ergebnisse der Physiologie,' "Theorie de Narkose," vol. 2, p. 666, 1902.

"On the Magnetic Changes of Length in Annealed Rods of Cobalt and Nickel." By Shelford Bidwell, M.A., Sc.D., F.R.S.

Received May 16,—Read June 2, 1904.

The dimensions of a piece of magnetic metal are, in general, changed by magnetisation. When subjected to a longitudinal field gradually increasing from a small value, an ordinary iron wire is at first extended, then, after passing a maximum, it recovers its original length, and finally becomes shorter than when unmagnetised.* In a paper communicated to the Society in 1894† I showed that the changes usually observed were modified if the iron had been annealed. In annealed iron the maximum extension is diminished and contraction begins in a weaker magnetic field; the elongation curve is, in fact, lowered to an extent dependent upon the completeness of the annealing. In the case of a certain soft-iron ring which had been raised to a bright red heat and allowed to cool slowly for about 14 hours, there was no preliminary elongation at all, retraction beginning (just as in nickel) with a very small magnetising force. It is of interest to note that after the lapse of 10 years the ring still retains its peculiar quality; on May 9, 1904 a perceptible diminution of its diameter was observed with a force of no more than 3 C.G.S. units, the diminution, of course, becoming greater with stronger forces. An unannealed ring of the same iron attained its greatest elongation, 33 ten-millionths, in a field of 80, and did not begin to contract until the field reached 420.

In the course of some recent work it became desirable to ascertain whether the changes of length exhibited by magnetised cobalt were analogously affected. Cobalt in the ordinary condition behaves oppositely to iron, contracting in weak fields and lengthening in strong ones. It might be expected, therefore, that if the metal were annealed it would begin to lengthen at an earlier stage of the magnetisation, possibly without any initial contraction. In searching the literature of the subject before undertaking the experiment, I found a very interesting paper by the Japanese physicists Honda and Shimizu entitled "Change in Length of Ferromagnetic Substances under High and Low Temperatures by Magnetisation."‡ Among the numerous curves given are two showing the changes of length produced by magnetisation in "cast cobalt" and "annealed cobalt" at ordinary temperatures. The curve for "cast cobalt" is of the same character as the one published by myself 16 years ago* (curve (*a*), fig. 1); that for "annealed cobalt" is an almost straight line, lying, however, not above, but below the axis of H; up to the field of 800 units, at which the experiment was stopped, there is no evidence that the contraction was tending to a limit. The authors make no comment whatever upon this remarkable effect, which may perhaps be well known in Japan, though I have never seen any reference to it in European publications.

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* Bidwell, 'Phil. Trans.,' A, 1888, p. 205.

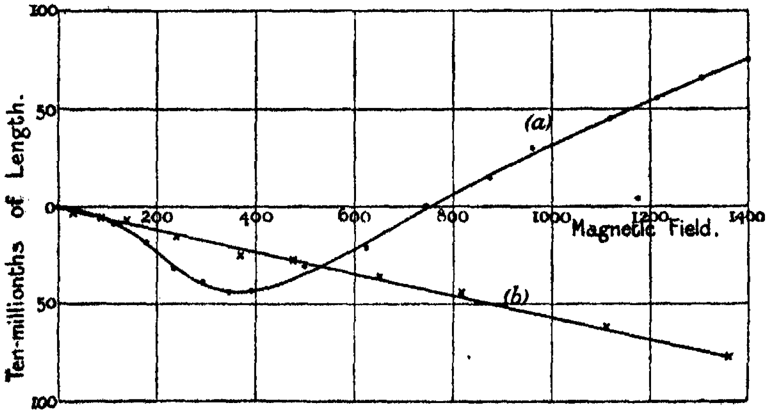
† 'Proc. Roy. Soc.,' vol. 55, p. 228.

‡ 'Tōkyō Sūgaku-Buturigakkwai Hōkoku,' No. 19, p. 197. The authors were good enough to send me a copy of the paper in 1903; unfortunately it was not read with the care it deserved until May, 1904.

The experiments described in the present paper were made with two different samples of cobalt, the one a cast rod, 9 cm. long and 0·56 cm. in diameter, the other a rolled strip, 10 cm. in length, 0·6 cm. in width and 0·08 cm. in thickness. These were enclosed in porcelain tubes, and placed side by side in the middle of a hot fire, not being removed until the fire had died out some 5 or 6 hours later.

In fig. 1, curve (*b*) shows the result of an experiment with the annealed cast cobalt. It will be noticed that the points of observation appear to indicate a slight sinuosity, but hardly greater than might be accounted for by experimental errors; a straight line drawn from the origin to the final point seems to pass evenly enough through the others. The curve agrees well with that given by Honda and Shimizu, and though the field was carried to a much higher value than was reached by them, there is still no sign that the contraction was approaching a limit. Curve (*a*), fig. 1, shows the changes of length exhibited by another piece of the same cast cobalt when in the unannealed state.

FIG. 1.



Cast cobalt. (*a*) unannealed, (*b*) annealed.

The effect of annealing upon the rolled cobalt was altogether

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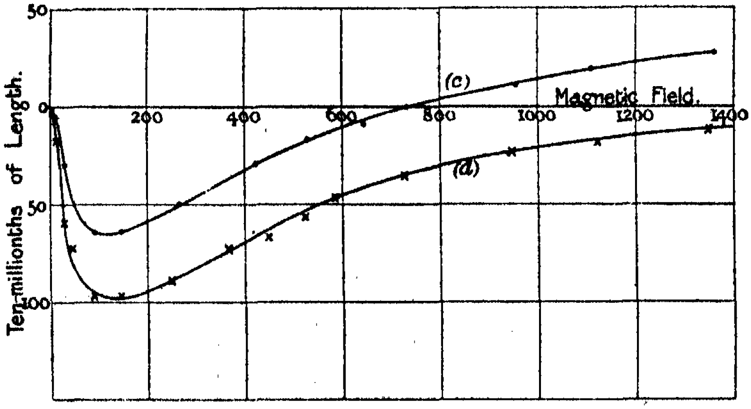
[*] 'Phil. Trans.,' *loc. cit.*

different. The behaviour of the unannealed piece is indicated by curve (*c*), fig. 2; it differs from that of the cast metal chiefly in the fact that the maximum retraction occurs in a much weaker field. The curve (*d*) for the annealed strip indicates a maximum retraction greater in degree, though it is reached in about the same field. The ascending limbs of the two curves are nearly parallel, but it is probable that the curve for the annealed strip would in very strong fields become asymptotic, never meeting the axis of H; an observation made with a field of 1750, 350 units beyond the limit of the diagram, showed that the retraction was still 9 ten-millionths of the length.

FIG. 2.

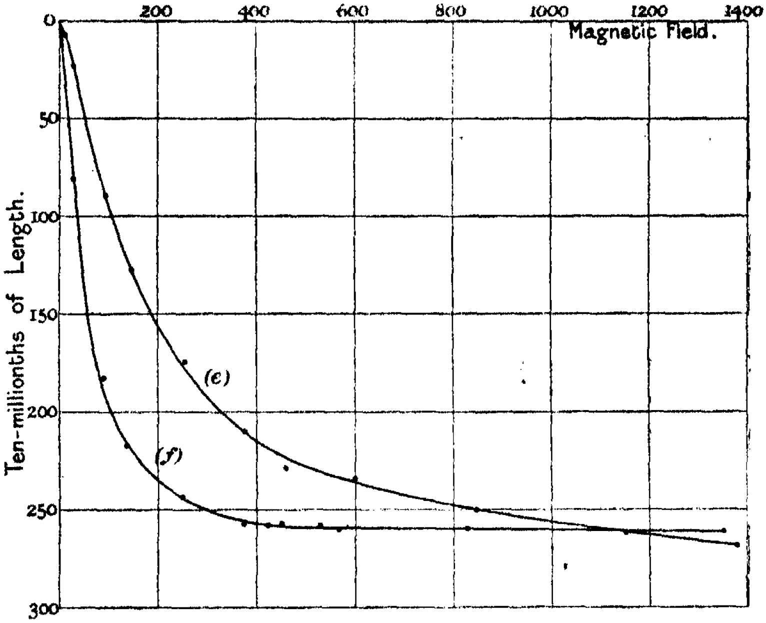


Rolled cobalt. (*c*) unannealed, (*d*) annealed.

The results of two experiments made with nickel before and after annealing are given in curves (*e*) and (*f*), fig. 3. The piece used was a thick wire 9 cm. in length and 0·35 cm. in diameter. After the first series of observations had been made, the wire was annealed in exactly the same manner as the cobalt, and again tested, with the result shown in curve (*f*). The modification effected in the form of the retraction curve is quite similar to that which annealing produces in the curve of magnetisation, and is probably due to nothing more than increased magnetic susceptibility. No such simple explanation can of course be given of the changes which are brought about in the behaviour of iron and cobalt. The fact that the two nickel curves intersect in a field of 1150 units may be merely an effect of temperature. The magnetic retraction of nickel is, as I have remarked in former papers, sensibly affected by small changes of temperature, and the intersection would be accounted for if the annealed wire happened to be a few degrees warmer than the unannealed.

As a consequence of the reciprocal relation between the changes of

FIG. 3.



Drawn nickel. (*e*) unannealed, (*f*) annealed.

length produced by magnetisation, and the changes of magnetisation attending mechanical strain,* it may be inferred that there would be no Villari reversal in well-annealed iron, like that of which the ring above referred to consisted, nor in annealed cast cobalt. In the rolled cobalt, however, to which the curves in fig. 2 relate, it might be expected that the effect would be considerably increased by annealing.

* J. J. Thomson, 'Applications of Dynamics to Physics and Chemistry,' pp. 47—59.

“A Generalisation of the Functions $\Gamma(n)$ and x^n.”

By Rev. F. H. Jackson, R.N. Communicated by Professor J. Larmor, Sec. R.S.

Received December 7,—Read December 10, 1903. Received in revised form June 15, 1904.

Contents.

Introduction; § 1. Difference-equation of the generalised gamma-function; § 2. Weierstrassian forms of the function; § 3. Extension of the multiplication-theorem of Gauss and Legendre; § 4. Definition of $(x)_n$; § 5. Extension of Lommel's product of two Bessel functions; § 6. The generalisation of the Beta function; § 7. Multiplication-theorem; § 8. Logarithmic derivatives and other series; § 9. The form of a generalised G function.

It is interesting to develope from simple principles a generalisation of the functions x^n and $\Gamma(n)$. Consider an infinite sequence $(1, p, p^2, p^3, \ldots p^n, \ldots)$, then write

$$
\begin{aligned}
[1] &= 1, \\
[2] &= 1+p, \\
\ldots &\quad \ldots \\
[n] &= 1+p+p^2+\ldots+p^{n-1} \text{ (n positive and integral),} \\
[-n] &= -p^{-1}-p^{-2}- \ldots -p^{-n} \text{ (n integral).}
\end{aligned}
$$

In general for all values of x, we take $[x] = (p^x-1)/(p-1)$. The object of this note is to carry on this extension, to determine the generalised forms of the gamma function, and to investigate some of its properties.

1. Consider the expression

$$[1][2][3]\ldots[n] = [n]!.$$

We can form a function $[n]!$ in general, which is

$$\Gamma_p([n+1]) = \underset{\kappa=\infty}{\mathrm{L}} \frac{[1][2][3]\ldots[\kappa]}{[n+1][n+2][n+3]\ldots[n+\kappa]}[\kappa]^n p^{\frac{1}{2}n(n+1)} \quad (p>1) \qquad \ldots\ldots\ldots\ldots\ldots \quad (1).$$

The infinite product is convergent if $p>1$. Wherever in this expression terms of the type p^x occur, the principal value of p^x alone is meant. If n be a negative integer, the product is clearly divergent.

The Difference Equation.—We have

$$\Gamma_p([n+1]) = [n]\,\Gamma_p([n]) \times \underset{\kappa=\infty}{\mathrm{L}} \frac{[\kappa]}{[n+\kappa]} p^n.$$

But $$\underset{\kappa=\infty}{\mathrm{L}} \frac{[\kappa]}{[n+\kappa]} p^n = \underset{\kappa=\infty}{\mathrm{L}} \frac{p^\kappa-1}{p^{n+\kappa}-1} p^n = 1 \ (p>1) = p^n \ (p<1).$$

Therefore

$$\Gamma_p([n+1]) = [n \; \Gamma_p([n]) \quad (p>1).$$

Since the infinite product (1) is also convergent, if $p<1$, the expression for the function in this case is

$$\Gamma_p([n+1]) = \underset{\kappa=\infty}{\mathrm{L}} \frac{[1][2][3]\ldots[\kappa]}{[n+1][n+2]\ldots[n+\kappa]}[\kappa]^n \quad (p<1) \quad \ldots \; (2).$$

In the limit when $p=1$, these expressions (1) and (2) reduce to Gauss's expression for Euler's gamma function.

2. *The Weierstrassian Form for the Function*—We obtain without difficulty from (1) that

$$\Gamma_p([x]) = p^{\frac{1}{2}x(x-1)}\frac{1}{[x]}\underset{\kappa=\infty}{\mathrm{L}}\left\{e^{x\left(\log[\kappa+1]-\kappa\log p-1-\frac{1}{[2]}-\frac{1}{[3]}-\ldots-\frac{1}{[\kappa]}\right)}\right\}$$

$$\prod_{s=1}^{s=\kappa}\left\{\left(1+p^{-x}\frac{[x]}{[s]}\right)^{-1}e^{\frac{x}{[s]}}\right\} \quad \ldots\ldots\ldots \quad (3).$$

Since $p>1$,

$$\underset{\kappa=\infty}{\mathrm{Limit}}\left\{\log\frac{[\kappa+1]}{p^\kappa}\right\} = \log_e\frac{p}{p-1},$$

also the series $1+\frac{1}{[2]}+\frac{1}{[3]}+\ldots$ is absolutely convergent, so that we finally write

$$\frac{1}{\Gamma_p([x])} = p^{\frac{1}{2}x(1-x)}[x]\,e^{\mathrm{P}x}\prod_{s=1}^{=\infty}\left\{\left(1+p^{-x}\frac{[x]}{[s]}\right)e^{-\frac{x}{[s]}}\right\},$$

in which

$$\mathrm{P} = 1+\frac{1}{[2]}+\frac{1}{[3]}+\ldots \textit{ad inf.} - \log_e\frac{p}{p-1}.$$

In the case when $p<1$

$$\frac{1}{\Gamma_p([x])} = [x]\,e^{\mathrm{Q}x}\prod_{s=1}^{s=\infty}\left\{\left(1+p^s\frac{[x]}{[s]}\right)e^{-\frac{p^s}{[1]}x}\right\} \quad \ldots\ldots\ldots \quad (4).$$

$$\mathrm{Q} = p+\frac{p^2}{[2]}+\frac{p^3}{[3]}+\ldots \textit{ad inf.} - \log_e\frac{1}{1-p}.$$

P and Q are extended forms of Euler's constant γ.

3. *Multiplication Theorem.*—Since $\Gamma_{p^{\frac{1}{n}}}([nx+n])$ may be written $\frac{q^{nx+n-1}-1}{q-1}\cdot\frac{q^{nx+n-2}-1}{q-1}\ldots\frac{q^{nx}-1}{q-1}\Gamma_q([nx])$, in which, for brevity, q denotes $p^{\frac{1}{n}}$, and $\frac{q^{nx+n-1}-1}{q-1} = \frac{\left[x+\frac{n-1}{n}\right]}{\left[\frac{1}{n}\right]}$ we have

$$\Gamma_{p^{\frac{1}{n}}}([nx+n]) = \left[x+\frac{n-1}{n}\right]\left[x+\frac{n-2}{n}\right]\ldots[x]\times\left[\frac{1}{n}\right]^{-n}\Gamma_{p^{\frac{1}{n}}}([nx]).$$

Let $f(x)$ denote

$$\frac{\Gamma_p([x])\,\Gamma_p\left(\left[x+\frac{1}{n}\right]\right)\ldots\Gamma_p\left(\left[n+\frac{n-1}{n}\right]\right)}{\Gamma_{p^{\frac{1}{n}}}([nx])}\times\frac{1}{\left[\frac{1}{n}\right]^{nx-1}},$$

then, by means of the difference equation, we obtain

$$f(x+1) = f(x).$$

If now throughout the infinite products, all expressions of the type $_p{}^x$ denote principal values only, then $f(x)$ is a single-valued function with a period unity, and for positive values of x has no singularities. It must therefore be a constant, and we find

$$f(x) = f\left(\frac{1}{n}\right) = \Gamma_p\left(\left[\frac{1}{n}\right]\right)\Gamma_p\left(\left[\frac{2}{n}\right]\right)\ldots\Gamma_p\left(\left[\frac{n-1}{n}\right]\right).$$

So that finally

$$\frac{\Gamma_p([x)]\,\Gamma_p\left(\left[x+\frac{1}{n}\right]\right)\ldots\Gamma_p\left(\left[x+\frac{n-1}{n}\right]\right)}{\left[\frac{1}{n}\right]^{nx-1}\Gamma_{p^{\frac{1}{n}}}([nx])}$$

$$= \frac{\varpi^{\frac{n-1}{2}}}{\sqrt{S\left(\frac{\omega}{n}\right)S\left(\frac{2\omega}{n}\right)\ldots S\left(\frac{\overline{n-1}\,\omega}{n}\right)}} \quad\ldots\ldots\quad (5),$$

$S(a)$ denoting a pseudo-periodic function analogous to $\sin a$. We define $S(a)$ as

$$\frac{\omega}{S(\omega a)} = \Gamma_p([a])\,\Gamma_p([1-a]), \qquad \omega^{\frac{1}{2}} = \Gamma_p([\tfrac{1}{2}]).$$

When $p = 1$, this theorem reduces to the multiplication-theorem of Gauss and Legendre.

4. In this article a generalisation of the function x^n will be formed by means of the generalised factorial Γ_p.

To deal with simple forms first. In $[n]!$ we replace p by p^2, and obtain

$$\frac{p^2-1}{p^2-1}\cdot\frac{p^4-1}{p^2-1}\ldots\frac{p^{2n}-1}{p^2-1} = \Gamma_{p^2}([n+1]) \quad (n \text{ positive and integral}),$$

so that

$$(1+p)(1+p^2)\ldots(1+p^n) = (p+1)^n\frac{\Gamma_{p^2}([n+1])}{\Gamma_p([n+1])}.$$

The expression $(1+p)(1+p^2)\ldots(1+p^n)$ is written $(2)_n$, this notation being both natural and convenient in investigating the properties of the generalised Bessel function*

$$J_{[n]}(x,\lambda) = \Sigma(-1)^s \frac{\lambda^{n+2r} x^{[n+2r]}}{[r]!\,[n+r]!\,(2)_r\,(2)_{n+r}}.$$

Similarly

$$(3)_n = (1+p+p^2)^n \frac{\Gamma_{p^3}([n+1])}{\Gamma_p([n+1])}.$$

When x and n are both positive integers,

$$(x)_n = (1+p+p^2+p^{x-1}) \frac{\Gamma_{p^x}([n+1])}{\Gamma_p([n+1])}.$$

The function we are seeking is clearly for all values of x and n (subject to limitations of convergence)—

$$(x)_n = [x]^n \frac{\Gamma_{p^x}([n+1])}{\Gamma_p([n+1])} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6),$$

which reduces if $p = 1$, to the function x^n.

5. *Extension of Lommel's product.*—

$$J_m(x)J_n(x) = \sum_{r=0}^{r=\infty}(-1)^r \frac{\binom{m+n+2r}{r}}{\Gamma(m+r+1)\,\Gamma(n+r+1)} \left(\frac{x}{2}\right)^{m+n+2r},$$

To illustrate the use of the function $(2)_n$, we take

$$J_{[n]}(x) = \sum_{r=0}^{r=\infty}(-1)^r \frac{x^{n+2r}}{[r]!\,[n+r]!\,(2)_r(2)_{n+r}},$$

$$\mathfrak{J}_{[m]}(x) = \sum_{r=0}^{r=\infty}(-1)^r \frac{x^{m+2r}}{[r]!\,[m+r]!\,(2)_r\,(2)_{m+r}} p^{2r(m+r)},$$

in which m and n are not restricted to integral values, so that $[n+r]!$ denotes $\Gamma_p([n+r+1])$. The function $\mathfrak{J}_{[m]}$ may be derived from $J_{[m]}$ by inverting the base p, when $J_{\overline{[m]}}$ becomes $p^{m^2}\mathfrak{J}_{[m]}\left(\frac{x}{p}\right)$. We proceed to show that

$$J_{[n]}(x)\,\mathfrak{J}_{[m]}(x)$$
$$= \Sigma(-1)^r \frac{\{2m+2n+4r\}!}{\{2m+2n+2r\}!\,\{2m+2r\}!\,\{2n+2r\}!\,\{2r\}!} x^{m+n+2r} \ldots\ldots \quad (7),$$

$\{2s\}!$ denoting $(2)_s\Gamma_p([s+1])$, or $[2]^s\,\Gamma_{p^2}([s+1])$.

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* 'Roy. Soc. Edin. Trans.,' vol. 41, part 1, Nos. (1), (6). 'Lond. Math. Soc. Proc.,' Series 2, vols. 1 and 2.

Multiplying together the two infinite series J and $\mathfrak{J}$, the coefficient of x^{m+n+2r} in the resulting series is

$$(-1)^r \sum_{s=0}^{s=r} p^{2s(m+s)} \frac{1}{\{2m+2s\}!\,\{2n+2r-2s\}!\,\{2r-2s\}!\,\{2s\}!} \quad \dots \quad (8).$$

We can sum this series of $r+1$ terms simply, as follows :—

In the case ($p = 1$), we see that the expression is Vandermonde's, and in the general case it is included under the following extension of Vandermonde's theorem

$$[x+y]_r = [x]_r + \sum_1^r p^{s(x-r+s)} \frac{[r]!}{[r-s]!\,[s]!} [x]_{r-s} [y]_s \quad \dots\dots \quad (9).$$

Substituting $m+r$ for x, $n+r$ for y, and changing the base p into p^2, we find

$$\{2m+2n+4r\}_r$$
$$= \{2m+2r\}_r + \sum p^{2s(m+s)} \frac{\{2r\}!}{\{2r-2s\}!\,\{2s\}!} \{2m+2r\}_{r-s} \{2n+2r\}_s \ (10),$$

in which, since $r-s$ is integral,

$\{2m+2r]_{r-s}$ denotes $[2m+2r]\,[2m+2r-2] \dots$ to $r-s$ factors.

Dividing both sides of (10) by $\{2m+2r\}!\,\{2n+2r\}!$ (m and n unrestricted) we obtain

$$\frac{\{2m+2n+4r\}_r}{\{2m+2r\}!\,\{2n+2r\}!\,\{2r\}!}$$
$$= \sum_{s=0}^{s=r} p^{2s(m+s)} \frac{1}{\{2m+2s\}!\,\{2n+2r-2s\}!\,\{2r-2s\}!\,\{2s\}!} \quad \dots \quad (11),$$

which series we have seen to be coefficient of x^{m+n+2r}, so that (7) is established. In the notation of the generalized gamma function

$$J_{[n]}(x)\,\mathfrak{J}_{[m]}(x) = \mathfrak{J}_{[n]}(x)\,J_{[m]}(x)$$
$$= \sum_{r=0}^{r=\infty} (-1)^r \frac{\Gamma_{p^2}([m+n+2r+1])}{\Gamma_{p^2}([m+n+r+1])\,\Gamma_{p^2}([m+r+1])\,\Gamma_{p^2}([n+r+1])\,\Gamma_{p^2}([r+1])}$$
$$\left(\frac{\lambda}{[2]}\right)^{m+n+2r} \quad \dots\dots\dots \quad (12).$$

By means of this product various series of squares of Bessel functions, and series of products of pairs of Bessel functions, may be generalized; for example,

$$\frac{2x}{\pi} = \{J_{\frac{1}{2}}\}^2 + 3\{J_{\frac{3}{2}}\}^2 + 5\{J_{\frac{5}{2}}\}^2 + \dots \quad \text{(Lommel.)}$$

corresponds to

$$\frac{x}{[2]}\left\{\frac{1}{\Gamma([\tfrac{3}{2}])}\right\}^2 = \Sigma p^{r(r-1)}\frac{[4r+2]}{[2]}\,J_{\left[\frac{2r+1}{2}\right]}(x)\,\mathfrak{J}_{\left[\frac{2r+1}{2}\right]}(x)\ldots \quad (13).$$

It is easily established that

$$J_{[n]}\mathfrak{J}_{[1-n]} + J_{[-n]}\mathfrak{J}_{[-1+n]} = \frac{[2]}{x\Gamma_{p^2}([n])\,\Gamma_{p^2}([1-n])} \quad \ldots \quad (14).$$

This reduces to

$$J_n J_{-n+1} + J_{-n} J_{n-1} = \frac{2}{\pi x}\sin n\pi.$$

As remarked in article (3) $\dfrac{1}{\Gamma_{p^2}([n])\,\Gamma_{p^2}([1-n])}$ is a pseudo-periodic function of n analogous to $\sin n\pi$. The period is given by

$$\omega^{\frac{1}{2}} = \Gamma_{p^2}([\tfrac{1}{2}]).$$

6. *The Function* $B_p([x][y])$.—Let $F([n-1]x^{p^m})$ denote the convergent infinite series

$$1 - p\frac{[n-1]}{[1]}x^{p^m} + \ldots + (-1)^r p^{r(r+1)/2}\frac{[n-1]\ldots[n-r]}{[r]!}x^{p^m[r]} + \ldots$$
$$\ldots\ldots\ldots\ldots \quad (15).$$

If $p = 1$, this series reduces to $(1-x)^{n-1}$.

Consider

$$p^{-m}\int_0^1 F([n-1]x^{p^m})\,x^{p[m-1]}dx = B_p([m],[n]) \quad \ldots\ldots \quad (16).$$

Integrating the series term by term, we obtain, after obvious reductions

$$\frac{p^{-m}}{[m]}\left\{1 + p^n\frac{[1-n][m]}{[1][m+1]} + p^{2n}\frac{[1-n][2-n][m][m+1]}{[1][2][m+1][m+2]} + \ldots\right\}.$$

The series within the large brackets is a particular case of Heine's series

$$1 + p^{\gamma-\alpha-\beta}\frac{[\alpha][\beta]}{[1][\gamma]} + \ldots = \prod_{n=0}^{\infty}\frac{[\gamma-\beta+n][\gamma-\alpha+n]}{[\gamma-\alpha-\beta+n][\gamma+n]}$$

$$= p^{\alpha\beta}\frac{\Gamma_p([\gamma-\alpha-\beta])\,\Gamma_p([\gamma])}{\Gamma_p([\gamma-\alpha])\,\Gamma_p([\gamma-\beta])} \quad (p>1),$$

whence

$$\frac{1}{p^{mn}}\frac{\Gamma_p([m])\,\Gamma_p([n])}{\Gamma_p([m+n])} = B([m],[n]) \quad \ldots\ldots\ldots\ldots \quad (17).$$

7. *The Multiplication Theorem for the Function* B_p:—

$$\frac{B_p([x],[\gamma])\ldots B_p\left(\left[x+\frac{n-1}{n}\right],[y]\right)}{B_{p^{\frac{1}{n}}}([y],[y])\ldots B_{p^{\frac{1}{n}}}([n-1\,.\,y],[y])}$$

$$= B_{p^{\frac{1}{n}}}([nx],[ny]) \times \frac{p^{(n-1)y(y-1)/2-nxy}}{\left\{\left[\frac{1}{n}\right]\left(\frac{1}{n}\right)_{y-1}\right\}^n} \;\ldots\ldots\; (18).$$

A particular case of this is

$$B_p([x],[x])\,B_p([x+\tfrac{1}{2}]\,[x+\tfrac{1}{2}]) = \frac{\{(\frac{1}{2})_{2x-1}\}^2\,\{\Gamma_p([\frac{1}{2}])\}^2}{[2x]}\,p^{-x^2-(x+\frac{1}{2})(x+\frac{1}{2})} \; (19).$$

If $p=1$, we obtain

$$B(x,x)\,B(x+\tfrac{1}{2},x+\tfrac{1}{2}) = \frac{\pi}{2^{4x-1}x} \quad \text{(Binet.)}$$

8. *The Logarithmic Derivatives of the Function* Γ_p.—From the expression

$$\{\Gamma_p([x])\}^{-1} = p^{\frac{1}{2}x(x-1)}\,[x]\,e^{Px}\prod_{s=1}^{s=\infty}\left\{\left(1+p^{-x}\frac{[x]}{[s]}\right)e^{-\frac{x}{[s]}}\right\} \quad (p>1)$$

we obtain

$$\frac{d}{dx}\{\log\Gamma_p([x])\} = -P-\tfrac{1}{2}\log p + x\log p - \frac{\log p}{(p-1)}\,\frac{p^x}{[x]}$$

$$+\sum_1^{\infty}\left\{\frac{1}{[s]}-\frac{\log p}{(p-1)}\,\frac{1}{[x+s]}\right\} \;\ldots\ldots\; (20).$$

From this

$$-P = \Gamma_p'([1]) + \tfrac{1}{2}\log p + \sum_{s=1}^{\infty}\left(1-\frac{\log p}{p-1}\right)\frac{1}{[s]}, \;\ldots\ldots\; (21);$$

which reduces when $p=1$ to $\Gamma'(1) = -\gamma$.

Similarly,

$$\left.\begin{aligned} \frac{d^2}{dx^2}\{\log\Gamma_p([x])\} &= \log p + \lambda^2\sum_{s=0}^{=\infty}\frac{p^{s+x}}{[s+x]^2} \\ \frac{d^3}{dx^3}\{\log\Gamma_p([x])\} &= \qquad -\lambda^3\sum\frac{p^{s+x}(p^{s+x}+1)}{[s+x]^3} \\ \frac{d^4}{dx^4}\{\log\Gamma_p([x])\} &= \qquad \lambda^4\sum\frac{p^{s+x}(p^{2s+2x}+4p^{s+x}+1)}{[s+x]^4} \\ \cdots\cdot & \qquad\qquad \cdots\cdot \\ \cdots\cdot & \qquad\qquad \cdots\cdot \end{aligned}\right\}\; (22).$$

$$\lambda = \frac{\log p}{p-1}.$$

Certain series of interest in connection with the function Γ_p are—

$$\frac{\Gamma_p([x])\,\Gamma_p([c+1])}{\Gamma_p([x+c])}$$

$$= \sum_{n=0}^{n=\infty}(-1)^n p^{\frac{n(n+1)}{2}-(n+1)c}\,\frac{[c]\,[c-1]\,[c-2]\ldots[c-n]}{[n]\,!}\,\frac{1}{[x+n]} \qquad (23),$$

$$\frac{\Gamma_p([x])}{\Gamma_p([x+\frac12])} = \frac{p^{\frac14}}{[\frac12]\,\Gamma_p([\frac12])}\,\sum\frac{[\frac12]\,[\frac32]\,[\frac52]\ldots[\frac{n-1}{2}]}{[n]\,!}\,\frac{1}{[x+n]} \qquad (24),$$

$$\frac{d}{dx}\log\frac{\Gamma_p([x+a])}{\Gamma_p([x])}$$

$$= a\log p+p^x\,[a]\left\{\frac{1}{[x]\,[x+a]}+\frac{1}{[x+1]\,[x+a+1]}+\ldots\right\}\frac{\log p}{(p-1)}$$

$$\ldots\ldots\ldots\ldots \quad (25).$$

$$= \log p+\lambda\sum(-1)^n\frac{[a]\,[a-1]\ldots[a-n+1]}{[x]\,[x+1]\ldots[x+n-1]}\,c_n.$$

$$c_n = \frac{1}{[n]}\left\{[n]\,p^{nx+\frac12 n(n-1)}-\frac{[n]\,[n-1]}{[2]\,!}\,p^{(n-1)x+\frac12(n-1)(n-2)}+\ldots+(-1)^n\right\}.$$

In case $p = 1$, the series (25) is

$$\frac{a}{x}-\frac12\,\frac{a(a-1)}{x(x+1)}+\frac13\,\frac{a(a-1)(a-2)}{x(x+1)(x+2)}-\ldots$$

9. *The Function* $G_p([x])$.—A function

$$G(x) = \underset{n=\infty}{L}\left[(n+1)^{\frac12(x-1)(x-2)}\,\{\Gamma(n+1)\}^{x-1}\prod_{\kappa=0}^{n-1}\frac{\Gamma(1+\kappa)}{\Gamma(x+\kappa)}\right] \qquad (26)$$

with the properties

$$G(x+1) = \Gamma(x)\,G(x), \quad G(1) = 1,$$

is given in Whittaker's *Modern Analysis*, p. 201, and is there referred to Alexeiewsky. This function has been discussed in detail in a more general form by E. W. Barnes.* From (26) we obtain without difficulty

$$G(x+1)$$

$$= \underset{\kappa=\infty}{L}\,\frac{\Gamma(1)\,\Gamma(2)\,\Gamma(3)\ldots\Gamma(\kappa)}{\Gamma(x+1)\,\Gamma(x+2)\,\Gamma(x+3)\ldots\Gamma(x+\kappa)}\,\{\Gamma(1+\kappa)\}^x\,(\kappa+1)^{\frac12 x(x-1)}.$$

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* 'Lond. Math. Soc. Proc.,' vol. 31, pp. 358 *et seq.*

Let us form a function

$$G_p([x+1]) = \mathop{L}_{\kappa=\infty} \frac{\Gamma_p([1])\,\Gamma_p([2])\,\ldots\,\Gamma_p([\kappa])}{\Gamma_p([x+1])\,\Gamma_p([x+2])\,\ldots\,\Gamma_p([x+\kappa])} \{\Gamma_p([\kappa+1])\}^x\,[\kappa+1]^{\frac{1}{2}x(x-1)}\,p^{\frac{1}{6}x(x-1)(x-2)} \ \ldots\ldots\ldots \quad (27).$$

We notice that this function will reduce, factor by factor, to $G(x)$, if we put $p = 1$.

Difference Equation.—

$$G_p([x+1]) = \Gamma_p([x])\,G_p([x]).$$

From the infinite product we have

$$\frac{G_p([x+1])}{G_p([x])} = \Gamma_p([x]) \times \mathop{L}_{\kappa=\infty} \frac{\Gamma_p([\kappa+1])}{\Gamma_p([\kappa+x])}\,[\kappa+1]^{\frac{1}{2}x(x-1)-\frac{1}{2}(x-1)(x-2)}\,p^{\frac{1}{6}x(x-1)(x-2)-\frac{1}{6}(x-1)(x-2)(x-3)}$$

$$= \Gamma_p([x])\,p^{\frac{1}{2}(x-1)(x-2)} \mathop{L}_{\kappa=\infty} \frac{\Gamma_p([\kappa+1])}{\Gamma_p([\kappa+x])}\,[\kappa+1]^{x-1}.$$

In the case $(p>1)$ the evaluation of the limit is not difficult, for since

$$\Gamma_p([\kappa+1]) = [1]\,[2]\,\ldots\,[\kappa],$$

the expression

$$p^{\frac{1}{2}(x-1)(x-2)} \mathop{L}_{\kappa=\infty} \frac{\Gamma_p([\kappa+1])}{\Gamma_p([\kappa+x])}\,[\kappa+1]^{x-1}$$

$$= L\,\frac{[\kappa+x]\,[\kappa+x+1]\,\ldots\,[\kappa+x-1+\kappa]}{[\kappa]^{x+\kappa-1}}\,[\kappa+1]^{x-1}\,p^{\frac{1}{2}(x^2-3x+2-\kappa^2-2\kappa x-x^2+\kappa+x)}$$

$$= L\left\{\frac{[\kappa+x]}{[\kappa]}\ldots\frac{[2\kappa+x-1]}{[\kappa]}\right\}\left(\frac{[\kappa+1]}{[\kappa]}\right)^{x-1} p^{\frac{1}{2}(2-2x-2\kappa x-\kappa^2+\kappa)}$$

$$= L\,\{p^{x+\overline{x+1}+x+2+\,\ldots\,\overline{x+\kappa-1}} \times p^{x-1} \times p^{1-x-\kappa x-\frac{1}{2}(\kappa^2+\kappa)}\} = p^0 = 1,$$

so that

$$G_p([x+1]) = \Gamma_p([x])\,G_p([x]) \ \ldots\ldots\ldots\ldots\ldots \quad (28).$$

"The Advancing Front of the Train of Waves emitted by a Theoretical Hertzian Oscillator." By A. E. H. Love, F.R.S., Sedleian Professor of Natural Philosophy in the University of Oxford. Received May 9,—Read June 2, 1904.

[Plates 2—6.]

The waves emitted by Hertz's oscillator have been identified with those due to a vibrating electric doublet, that is to say, to a singular point (of a certain type) of the electromagnetic equations. In air or in free æther these equations may be written in the forms

$$\left.\begin{aligned} \frac{1}{\mathrm{c}}\frac{\partial}{\partial t}(\mathrm{X}, \mathrm{Y}, \mathrm{Z}) &= \operatorname{curl}(\alpha, \beta, \gamma) \\ -\frac{1}{\mathrm{c}}\frac{\partial}{\partial t}(\alpha, \beta, \gamma) &= \operatorname{curl}(\mathrm{X}, \mathrm{Y}, \mathrm{Z}) \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (1),$$

in which c is the velocity of radiation, (X, Y, Z) denotes the electric force measured in electrostatic units, (α, β, γ) denotes the magnetic force measured in electromagnetic units. These equations are nearly identical with those which have been used by Hertz.* They differ from the latter in that c is here written for the quantity which Hertz wrote 1/A, and they differ also in the signs of the right-hand members. The reason for the latter difference is that Hertz used a left-handed system of axes of x, y, z; but it is on many grounds more convenient to use a right-handed system, as will be done here. The field due to a variable doublet at the origin, with its axis parallel to the axis of z, is expressed by equations of the form

$$\left.\begin{aligned} (\mathrm{X}, \mathrm{Y}, \mathrm{Z}) &= \left(\frac{\partial^2}{\partial x \partial z}, \frac{\partial^2}{\partial y \partial z}, -\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2}\right)\frac{\psi(\mathrm{c}t - r)}{r} \\ (\alpha, \beta, \gamma) &= \frac{1}{\mathrm{c}}\left(\frac{\partial^2}{\partial y \partial t}, -\frac{\partial^2}{\partial x \partial t}, 0\right)\frac{\psi(\mathrm{c}t - r)}{r} \end{aligned}\right\} \quad \ldots \quad (2),$$

in which r denotes the distance of any point (x, y, z) from the origin, and ψ ($\mathrm{c}t$) is the moment of the doublet at time t. In Hertz's work the function ψ is taken to be a simple harmonic function of its argument, and written in a form equivalent to $\mathrm{E}l \sin n\,(t - r/\mathrm{c})$. This supposition would be adequate if the vibrations were maintained, or if the damping due to radiation were very slight. The actual damping of Hertz's oscillator has been investigated experimentally by V. Bjerknes,* and shown to be very considerable. Accordingly, we ought to take for ψ a function of the form

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* "Die Kräfte elektrischer Schwingungen, behandelt nach der Maxwell'schen Theorie," 'Ann. Phys. Chem.' (Wiedemann), vol. 36 (1888). Reprinted in Hertz, 'Untersuchungen ü. d. Ausbreitung d. elektrischen Kraft' (Leipzig, 1892), p. 147, and in 'Electric Waves' (English edition), p. 137. The detailed references in the text are to the pages of the English edition.

$$\psi = \mathrm{A}e^{-\frac{\nu}{\lambda}(\mathrm{C}t-r)} \sin \frac{2\pi}{\lambda}(\mathrm{C}t - r + \epsilon) \qquad (3),$$

where λ is the wave-length, A a constant depending upon the amplitude of the vibrations, ϵ a constant expressing the phase, and ν a constant expressing the damping. According to the experiments of Bjerknes already cited, ν may be taken to be about 0·4 when the wave-length λ is about 10 m. The effect of the introduction of the exponential factor into the expression for ψ has been investigated in an elaborate memoir by K. Pearson and A. Lee.† In that memoir it is supposed that the fixed epoch from which time is measured is the instant at which the vibrations begin, so that, at any instant, the field expressed by (2) and (3) is confined to the region within the sphere $r = \mathrm{C}t$. In the expression for ψ the phase-constant ϵ is omitted by these authors. They have thus tacitly assumed that ψ vanishes at the front of the advancing wave.

This front is a moving surface which is a surface of discontinuity in regard to the electric and magnetic forces. Within the surface these forces are expressed by the formulæ already written down; outside the surface they must be expressed by some other formulæ. The waves, in fact, advance either through a pre-established electrostatic or electromagnetic field of some kind, or possibly through a region of space in which there is no electric or magnetic force. Whatever view may be taken of the nature of the field outside the wave-front, definite conditions must be satisfied at this surface. These conditions are known, but they have not been applied to the problem in hand. It seems worth while to make this application, and, in particular, to ascertain the effect of these conditions in modifying the results obtained by Pearson and Lee.

Let Σ denote in general a moving surface which separates two electromagnetic fields. Then it is known that Σ moves normally to itself with the velocity C. Let $(\mathrm{X}_0, \mathrm{Y}_0, \mathrm{Z}_0)$ and $(\alpha_0, \beta_0, \gamma_0)$ denote the electric and magnetic forces on that side of Σ towards which Σ advances, let l, m, n denote the direction cosines of the normal to Σ drawn towards this side, and let $(\mathrm{X}, \mathrm{Y}, \mathrm{Z})$ and (α, β, γ) denote the electric and magnetic forces on the other side. Then at any point of Σ it is known that the following six equations must be satisfied:—

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* 'Ann. Phys. Chem.' (Wiedemann), vol. 44 (1891).

† 'Phil. Trans.,' A, vol. 193, 1900.

$$\begin{aligned} X - X_0 &= n(\beta - \beta_0) - m(\gamma - \gamma_0), & \alpha - \alpha_0 &= m(Z - Z_0) - n(Y - Y_0), \\ Y - Y_0 &= l(\gamma - \gamma_0) - n(\alpha - \alpha_0), & \beta - \beta_0 &= n(X - X_0) - l(Z - Z_0), \\ Z - Z_0 &= m(\alpha - \alpha_0) - l(\beta - \beta_0). & \gamma - \gamma_0 &= l(Y - Y_0) - m(X - X_0), \end{aligned} \quad \ldots\ldots\ldots\ldots (4).$$

These equations may be expressed in words in the statements that the components of electric and magnetic force along the normal to Σ are continuous, and that the discontinuities of the tangential components of the electric and magnetic forces are equal in magnitude and are directed along lines at right angles to each other in such a way that the discontinuity of electric force, the discontinuity of magnetic force, and the normal to the surface, in this order, are parallel to the axes of x, y, z in a right-handed system.[*] The case in which there is no electric or magnetic force on the side of Σ towards which it advances is included by putting (X_0, Y_0, Z_0) and $(\alpha_0, \beta_0, \gamma_0)$ equal to zero, and the case in which the field on this side of the surface is electrostatic is included by putting $(\alpha_0, \beta_0, \gamma_0)$ equal to zero.

The conditions (4) have been established by a rather troublesome process which may be replaced by the following simpler argument:—The ordinary equations (1) of the field fail at the surface of discontinuity Σ through the infinity of some of the differential coefficients $\partial x/\partial t$, ... Consider the axis of x to be parallel to the normal to Σ at a point P. Then as Σ passes over P the state of the medium at P changes from that expressed by $(X_0, \ldots \alpha_0, \ldots)$ to that expressed by $(X, \ldots, \alpha, \ldots)$. Suppose the change to take place in a very short time δt, and multiply both sides of the equations (1) by $c\delta t$. Then in the left-hand members we must write $X - X_0$ for $\frac{\partial X}{\partial t}\,\delta t$, and similarly for the other quantities of the same kind. Again, we may put $c\delta t = \delta x$, where δx is the distance over which the small part of Σ near to P moves in the interval δt; and then the limit of $\frac{\partial \beta}{\partial x}\,c\delta t$ or $\frac{\partial \beta}{\partial x}\,\delta x$ is the difference of the values of β just before and just behind the surface Σ, or it is $\beta_0 - \beta$. The limits of such quantities as $\frac{\partial \alpha}{\partial y}\,c\delta t$, in which the differentiation is performed with respect to any co-ordinate other than x, are zero.

From the six equations (1) we deduce in this way the six equations

$$\begin{aligned} X - X_0 &= 0, & Y - Y_0 &= -(\gamma_0 - \gamma), & Z - Z_0 &= \beta_0 - \beta, \\ \alpha - \alpha_0 &= 0, & -(\beta - \beta_0) &= -(Z_0 - Z), & -(\gamma - \gamma_0) &= Y_0 - Y. \end{aligned}$$

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[*] These results were given effectively in a paper by the author in 'Proc. London Math. Soc.' (Ser. 2), vol. 1, p. 37 (1903). Equivalent conditions appear to have been employed by O. Heaviside, 'Electrical Papers,' vol. 2, pp. 405 *et seq.*

These equations express the same relations between the forces and the direction of the normal to Σ as are expressed by (4).

In the application of conditions (4) to the problem of the Hertzian oscillator, the external field (X_0, Y_0, Z_0), $(\alpha_0, \beta_0, \gamma_0)$ is that which is established at the instant when the vibrations begin. At this instant the brass balls of the oscillator are so highly charged that the electric strength of the air between them gives way. The initial field is that due to the charges at this instant, so that it can most appropriately be represented as the electrostatic field of a fixed doublet. If B denotes the moment of this doublet, the field in question is expressed by the equations

$$\left.\begin{aligned} (X_0, Y_0, Z_0) &= \left(\frac{\partial^2}{\partial x \partial z}, \frac{\partial^2}{\partial y \partial z}, \frac{\partial^2}{\partial z^2}\right)\frac{B}{r} \\ (\alpha_0, \beta_0, \gamma_0) &= 0 \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (5).$$

Now write down the complete expressions for X, Y, Z, and α, β, γ, in accordance with equations (2). Denoting differential coefficients of the function ψ with respect to its argument by accents, these expressions are

$$\left.\begin{aligned} X &= \frac{xz}{r^5}(3\psi + 3r\psi' + r^2\psi''), \qquad Y = \frac{yz}{r^5}(3\psi + 3r\psi' + r^2\psi''), \\ Z &= -\frac{x^2+y^2}{r^5}(3\psi + 3r\psi' + r^2\psi'') + \frac{2}{r^3}(\psi + r\psi'), \\ \alpha &= -\frac{y}{r^3}(\psi' + r\psi''), \qquad \beta = \frac{x}{r^3}(\psi' + r\psi''), \qquad \gamma = 0, \end{aligned}\right\} \quad (6).$$

In like manner, complete expressions for X_0, Y_0, Z_0, as given by (5), are

$$X_0 = \frac{xz}{r^5}3B, \qquad Y_0 = \frac{yz}{r^5}3B, \qquad Z_0 = -\frac{x^2+y^2}{r^5}3B + \frac{2}{r^3}B, \ldots (7).$$

Let $t = 0$ be the instant when the vibrations begin. Then $r = Ct$ is the equation of the surface separating at time t the field expressed by (6) from that expressed by (7), and the direction cosines l, m, n of the normal to this surface are x/r, y/r, z/r. When these values of X,... are substituted in (4) it will be found that ψ'' disappears, and that the equations (4) give

$$3(\psi - \beta) + 2r\psi' = 0, \qquad 2(\psi - B) + 2r\psi' = 0,$$

which must hold when $r = Ct$, *i.e.*, when the argument of ψ is zero. Hence we must have

$$\psi(0) = B, \qquad \psi'(0) = 0.$$

Now take ψ to have the form (3). We find

$$A \sin\frac{2\pi\epsilon}{\lambda} = B, \qquad \tan\frac{2\pi\epsilon}{\lambda} = \frac{2\pi}{\nu} \ldots\ldots\ldots\ldots\ldots \quad (8).$$

The second of these equations determines ϵ and the first determines A in terms of B. It appears that B (the moment of the initial doublet) is the maximum moment of the vibrating doublet.*

It has now been shown that the waves expressed by (2) in which ψ is given by (3) *can* advance through the field expressed by (5), provided the constants A, B, ν, ϵ, are connected by the equations (8). Incidentally it has been shown that the waves expressed by (2) in which ψ is given by (3) cannot advance through a region in which there is no electric or magnetic force, and that the phase constant ϵ cannot vanish. In fact, the function ψ instead of vanishing at the front of the wave has there its numerically greatest value.

Expressions may be formed for the radial and transverse components of the electric force and for the magnetic force. The lines of electric force lie in planes through the axis of the doublet, and the lines of magnetic force are circles about that axis. The radial component R of the electric force is given by the equation

$$\begin{aligned}\mathrm{R} = \frac{2\cos\theta}{r^3}\mathrm{A}e^{-\frac{\nu}{\lambda}(\mathrm{C}t-r)}\Big[\Big(1-\frac{r\nu}{\lambda}\Big)\sin\frac{2\pi}{\lambda}(\mathrm{C}t-r+\epsilon)& \\ +\frac{2\pi r}{\lambda}\cos\frac{2\pi}{\lambda}(\mathrm{C}t-r+\epsilon)\Big] & \quad\ldots\ldots\quad (9),\end{aligned}$$

when $\mathrm{C}t > r$, but when $\mathrm{C}t < r$ we have

$$\mathrm{R} = \frac{2\cos\theta}{r^3}\mathrm{A}\sin\frac{2\pi\epsilon}{\lambda} \quad\ldots\ldots\ldots\ldots\ldots\ldots\quad (10),$$

θ being the angle which a line drawn from the origin to a point at distance r makes with the axis of the doublet.

The transverse component Θ of the electric force is given by the equation

$$\begin{aligned}\Theta = \frac{\sin\theta}{r^3}\mathrm{A}e^{-\frac{\nu}{\lambda}(\mathrm{C}t-r)}\Big[\Big(1-\frac{r\nu}{\lambda}+\frac{r^2(\nu^2-4\pi^2)}{\lambda^2}\Big)\sin\frac{2\pi}{\lambda}(\mathrm{C}t-r+\epsilon)& \\ +\frac{2\pi r}{\lambda}\Big(1-\frac{2r\nu}{\lambda}\Big)\cos\frac{2\pi}{\lambda}(\mathrm{C}t-r+\epsilon)\Big] & \quad\ldots\ldots\quad (11),\end{aligned}$$

when $\mathrm{C}t > r$, but when $\mathrm{C}t < r$ we have

$$\Theta = \frac{\sin\theta}{r^3}\mathrm{A}\sin\frac{2\pi\epsilon}{\lambda} \quad\ldots\ldots\ldots\ldots\ldots\ldots\quad (12).$$

---

* The result that the maximum moment of the vibrating doublet ought to be the same as the moment of the doublet existing at the instant when the vibrations begin is noted by M. Brillouin, 'Propagation de l'Électricité, Histoire et Théorie' (Paris, 1904), p. 313.

The magnetic force H is given by the equation

$$\mathrm{H} = -\frac{\sin\theta}{r^2}\mathrm{A}e^{-\frac{\nu}{\lambda}(\mathrm{C}t-r)}\left[\left(\frac{\nu}{\lambda}-\frac{r(\nu^2-4\pi^2)}{\lambda^2}\right)\sin\frac{2\pi}{\lambda}(\mathrm{C}t-r+\epsilon)\right.$$
$$\left.-\frac{2\pi}{\lambda}\left(1-\frac{2r\nu}{\lambda}\right)\cos\frac{2\pi}{\lambda}(\mathrm{C}t-r+\epsilon)\right] \quad\ldots\ldots\ldots\quad (13),$$

when $\mathrm{C}t > r$, but when $\mathrm{C}t < r$ it vanishes.

The radial electric force is continuous at the front of the wave, *i.e.*, at the surface $r = \mathrm{C}t$. The discontinuity of the transverse component of the electric force at the front of the wave is

$$\frac{\sin\theta}{r}\frac{\mathrm{A}}{\lambda^2}(\nu^2+4\pi^2)\sin\frac{2\pi\epsilon}{\lambda} \quad\ldots\ldots\ldots\ldots\ldots\ldots\quad (14),$$

and this is equal, as it should be, to the magnetic force at the front of the wave.

The lines of electric force are the intersections of the planes through the axis of the doublet with a certain family of surfaces $\mathrm{Q} = \text{constant}$.* If we denote by ρ the distance of a point from the axis, so that $\rho = r\sin\theta$, the quantity Q is $\rho\frac{\partial}{\partial\rho}\left(\frac{\psi}{r}\right)$, and the components of electric force parallel to the axis and at right angles to it are respectively $-\frac{1}{\rho}\frac{\partial\mathrm{Q}}{\partial\rho}$ and $\frac{1}{\rho}\frac{\partial\mathrm{Q}}{\partial z}$. The flux of electric force through any circle with its centre on the axis of the doublet may be expressed as $-2\pi\mathrm{Q}$. The form of Q is given by the equations

$$\mathrm{Q} = -\frac{\sin^2\theta}{r}\mathrm{A}e^{-\frac{\nu}{\lambda}(\mathrm{C}t-r)}\left\{\left(1-\frac{r\nu}{\lambda}\right)\sin\frac{2\pi}{\lambda}(\mathrm{C}t-r+\epsilon)\right.$$
$$\left.+\frac{2\pi r}{\lambda}\cos\frac{2\pi}{\lambda}(\mathrm{C}t-r+\epsilon)\right\} \quad\ldots\ldots\quad (15),$$

when $\mathrm{C}t > r$, and

$$\mathrm{Q} = -\frac{\sin^2\theta}{r}\mathrm{A}\sin\frac{2\pi\epsilon}{\lambda} \quad\ldots\ldots\ldots\ldots\ldots\ldots\quad (16),$$

when $\mathrm{C}t < r$. At the separating surface Q is continuous, just as the radial component R of electric force is continuous, and in fact we have

$$\mathrm{Q} = -\tfrac{1}{2}\frac{\sin^2\theta}{\cos\theta}r^2\mathrm{R} \quad\ldots\ldots\ldots\ldots\ldots\ldots\quad (17),$$

throughout the field.

The particular case where there is no damping by radiation is included in the foregoing by putting $\nu = 0$, $2\pi\epsilon/\lambda = \frac{1}{2}\pi$; and then we have

$$\psi = \mathrm{A}\cos\frac{2\pi}{\lambda}(\mathrm{C}t-r), \qquad \mathrm{B} = \mathrm{A}.$$

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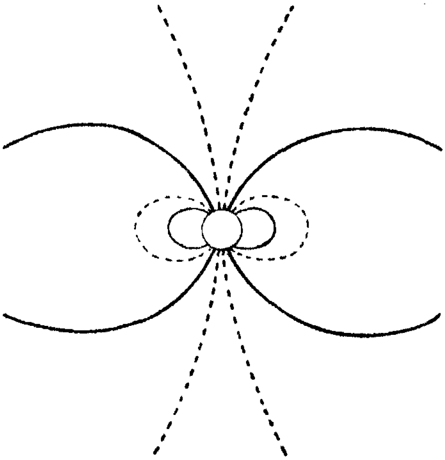
* The use of the function Q in these problems was initiated by Hertz, *loc. cit.*

This is the case discussed by Hertz, but his discussion has no very definite reference to the front of the waves. The field due to the initially existing doublet is the well-known electrostatic field of a doublet, the lines of electric force being identical with the lines of magnetic force due to a magnet or to an uniformly magnetised sphere, or with the lines of flow of incompressible fluid through which a sphere is moving. These lines have been traced often,[*] a few of them are traced in fig. A.

FIG. A.



Hertz[†] has figured the lines of force within a distance of $\frac{3}{4}\lambda$ of the oscillator at a number of instants during the progress of a vibration. It would be easy to determine the modifications that ought to be made in his figures on account of the existence of a front to the advancing wave-train and of the existence outside that front of an electrostatic field. The moment of the doublet which gives rise to this field is the maximum moment of the vibrating doublet. At any instant during the vibration the electromagnetic field of the vibrator will be established within a distance from the doublet equal to the distance which light would travel in the time that has elapsed since the commencement of the vibrations. After one-eighth of a period, for instance, this field will be confined to the region within a sphere of radius $\frac{1}{8}\lambda$, and outside this sphere the field is the above-described electrostatic field. It follows that, to obtain the lines of force during the first three-quarters of a period, a circle of suitable radius should be described round the centre of one of Hertz's figures, and the parts of his lines of force which lie outside that circle should be suppressed and their places taken by curves of the family traced in fig. A. The result that at the beginning of the vibration the moment of the doublet is a maximum would be expressed by taking his figures in the order 29, 30, 27, 28. After the electromagnetic field has become established, these figures represent the field near the vibrator at instants which are the beginning of a period, $\frac{1}{8}$ of a period later, $\frac{1}{4}$ of a period later, $\frac{3}{8}$ of a period later. If the arrow heads in his figures are reversed, they represent in the same order the field after $\frac{1}{2}$ a period, $\frac{5}{8}$ of a period, $\frac{3}{4}$ of a period, $\frac{7}{8}$ of a period from the beginning of a particular vibration, which is not the first vibration. To trace the course of the first vibration we should proceed as follows:—At the instant when the vibrations begin the field is that shown in fig. A. After $\frac{1}{8}$ of a period draw on Hertz's figure 30 a circle of radius $\frac{1}{8}\lambda$,* suppress the part of the figure outside this circle and replace it by the part of fig. A which is outside the same circle. To obtain the fields after $\frac{1}{4}$ period and $\frac{3}{8}$ period, similar work should be done upon Hertz's figures 27 and 28 with circles of radii $\frac{1}{4}\lambda$, $\frac{3}{8}\lambda$. After $\frac{1}{2}$ a period, reverse the arrow heads in Hertz's figure 29, draw on this figure a circle of radius $\frac{1}{2}\lambda$, suppress the part of the figure which is outside this circle and replace it by the part of fig. A which is outside the same circle. To obtain the fields after $\frac{5}{8}$ period, $\frac{3}{4}$ period, $\frac{7}{8}$ period, similar work should be done upon the figures 30, 27, 28 with circles of radii $\frac{5}{8}\lambda$, $\frac{3}{4}\lambda$, $\frac{7}{8}\lambda$. These modified figures have not been drawn here because a similar procedure will be adapted presently to the figures of Pearson and Lee in which account is taken of the damping by radiation.

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[*] See, *e.g.*, J. J. Thomson, 'Elements of Electricity and Magnetism,' p. 223, Lamb, 'Hydrodynamics,' p. 137.

[†] 'Electric Waves,' pp. 144, 145. The figures are reproduced by M. Brillouin, *loc. cit.*, pp. 292, 293; and by A. Gray, 'Magnetism and Electricity,' vol. 1 (London, 1898), pp. 406—408.

The notation of this paper can be identified with that of Pearson and Lee by means of the equations

$$t' = t + \epsilon/\mathrm{C}, \quad \mathrm{E}l = -\mathrm{A}e^{\nu\epsilon/\lambda}, \quad 2\tau = \lambda/\mathrm{C}, \quad \chi = \frac{\pi}{2} - \frac{2\pi\epsilon}{\lambda} \quad \ldots \quad (18),$$

in which the quantities $\mathrm{E}l$, τ, χ are used by these authors,† and t' is the quantity which they denote by t. They have traced the lines of electric force, given by Q = constant, for certain chosen values of Q, for a region of space between the spheres $r = \frac{1}{10}\lambda$ and $r = \frac{5}{4}\lambda$, and for fifty-six values of t', viz.: $t' = 2\tau\,(\frac{1}{8}, \frac{1}{4}, \ldots 7)$. The chosen values of Q are such that $\mathrm{Q}\lambda/2\pi\mathrm{E}l = \pm\frac{1}{100}, \pm\frac{1}{10}, \pm\frac{3}{10}, \pm\frac{1}{2}$. The curves thus formed are shown in their Plates 1—7, each plate containing eight figures.‡ The chosen value of ν is 0·4.

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* In Hertz's notation it would be $\frac{1}{4}\lambda$. Hertz has used the letter λ to denote the half wave-length.

† 2τ is the period.

‡ A number of these figures have been reproduced by M. Brillouin in plates at the end of his treatise already cited.

The lines of force drawn in some of these figures need some modification on account of the existence of a front of the wave-train. At any instant the electromagnetic field that is propagated with the waves will have reached a distance Ct from the oscillator, and therefore those parts only of the curves which lie within circles of radii $\lambda(t'/2\tau - \epsilon/\lambda)$ are lines of force in the actual vibrations. Outside spheres having these radii the actual field is the electrostatic field due to the fixed doublet, viz.: it is the field expressed by (5) and figured in fig. A. In the notation of (18) the lines of force in this field are given by the equation

$$\frac{Q\lambda}{2\pi El} = \frac{\sin^2\theta}{r}\frac{\lambda}{2\pi}e^{-\nu\epsilon/\lambda}\sin\frac{2\pi\epsilon}{\lambda}.$$

The continuations of the lines of force outside the wave-fronts at the various times in question are obtained by equating this expression to the values $\pm\frac{1}{100}$, $\pm\frac{1}{10}$, $\pm\frac{3}{10}$, $\pm\frac{1}{2}$. The heavy dotted, heavy continuous, fine dotted and fine continuous curves in fig. A have been drawn to correspond with these four pairs of values, λ being represented by 1 inch (= 2·54 cm.).

The value of ν being 0·4, the following numerical values are found for the various quantities :—

$$\tan\frac{2\pi\epsilon}{\lambda} = 5\pi, \qquad \frac{2\pi\epsilon}{\lambda} = 1{\cdot}5071389, \qquad \frac{\epsilon}{\lambda} = 0{\cdot}239868,$$

$$\frac{\nu\epsilon}{\lambda} = 0{\cdot}0959474, \qquad e^{-\nu\epsilon/\lambda} = 0{\cdot}908512, \qquad e^{-\nu\epsilon/\lambda}\sin\frac{2\pi\epsilon}{\lambda} = 0{\cdot}906676,$$

$$2\pi e^{\nu\epsilon/\lambda}\operatorname{cosec}\frac{2\pi\epsilon}{\lambda} = 6{\cdot}99403.$$

The circles outside which the lines of force drawn in the figures of Pearson and Lee have to be replaced by other lines are given by the equation

$$r = \lambda(a - 0{\cdot}239868) \qquad \text{.....................} \qquad (19),$$

in which a has the values $\frac{1}{8}$, $\frac{1}{4}$, ... In fig. 1 of their Plate 1, r would be negative; this figure, in fact, relates to an epoch before the vibrations begin, and no part of it represents lines of force that are formed. In fig. 2 of their Plate 1, r would be about $\frac{1}{100}$ of a wave-length, so that the circle is too small to be drawn. In fig. 3 of their Plate 1, $r = 0{\cdot}135$ of a wave-length, so that the front of the waves cannot be distinguished clearly from the inner circular boundary of the figure. Those parts only of the lines drawn in this figure which lie between the inner circular boundary and a circle of radius $(0{\cdot}135)\,\lambda$ are actual lines of force at the instant in question. Figs. 1, 2, and 3 of Plate 1 should, therefore, be omitted. In the remaining figures of Plate 1, and in figs. 9, 10 and 11 of Plate 2, parts only of the lines of force that are drawn are actual lines of force at the corresponding instants during the vibrations. These parts lie within the circles obtained from (19) by giving to a the values $\frac{1}{2}$, $\frac{5}{8}$, ... $\frac{11}{8}$, and the corresponding instants are $t = (0{\cdot}26,\ 0{\cdot}385,\ 0{\cdot}51,\ 0{\cdot}635,\ 0{\cdot}76,\ \ldots 1{\cdot}135) \times (\text{period})$. The corresponding lines of force outside these circles are given by the equation

$$\frac{\sin^2\theta}{r} = \frac{1}{\lambda}(6{\cdot}99403)\,b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (20),$$

in which b has the values $\pm\frac{1}{100}$, $\pm\frac{1}{10}$, $\pm\frac{3}{10}$, $\pm\frac{1}{2}$. These are the curves drawn in fig. A above. The remaining figures (12—56) of Plates 2—7 are unaffected by the conditions that hold at the front of the waves. The figures by which Pearson and Lee's figs. 4—11 of their Plates 1 and 2 should be replaced are the figures numbered 4—11 on Plates 2—5 accompanying this paper.

In these figures the fine continuous circle represents the wave-front at the time $t\ [= t' - (0{\cdot}24)2\tau]$. The discontinuity of the electric field at the wave-front is shown by the change of direction of the lines of force at this circle. Those lines of force which are determined by putting $\dfrac{Q\lambda}{2\pi El}$ equal to $\pm\frac{1}{100}$, $\pm\frac{1}{10}$, $\pm\frac{3}{10}$, and $\pm\frac{1}{2}$, are shown by the heavy dotted, heavy continuous, fine dotted, and fine continuous lines respectively. The dotted circles that lie within the fine continuous circle are curves at which Q vanishes, or the electric force has no radial component. A surface $Q = 0$ travels outwards at a varying rate so as to lie within the wave-front $r = Ct$ and to tend to overtake it as t increases. This is shown by the inner dotted circles in figs. 5—8, and by the outer dotted circles which in figs. 9—11 lie within the fine continuous circle. It appears that no spherical surface of the set given by $Q = 0$ is the front of the advancing wave-train, but that one of these surfaces tends to coincidence with this front as the wave-train advances.

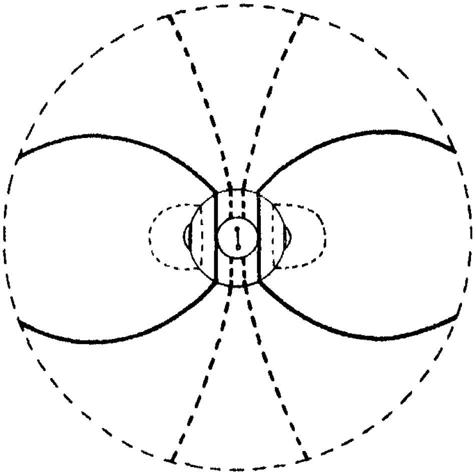
The discontinuity of the electromagnetic field may also be shown in a striking manner by tracing curves to represent at particular instants the values of the transverse component Θ of the electric force, which correspond with all values of r, the distance of a point from the oscillator. Consider points in the equatorial plane of the oscillator, for which $\theta = \frac{1}{2}\pi$. The form of Θ as a function of r is determined by the equations

$$\Theta = \frac{A}{r^3} e^{-\frac{\nu}{\lambda}(Ct-r)} \left[\left(1 - \frac{r\nu}{\lambda} - \frac{r^2(4\pi^2 - \nu^2)}{\lambda^2}\right) \sin\frac{2\pi}{\lambda}(Ct - r + \epsilon) \right.$$
$$\left. + \frac{2\pi r}{\lambda}\left(1 - \frac{2r\nu}{\lambda}\right)\cos\frac{2\pi}{\lambda}(Ct - r + \epsilon)\right],$$

when $Ct > r$, and

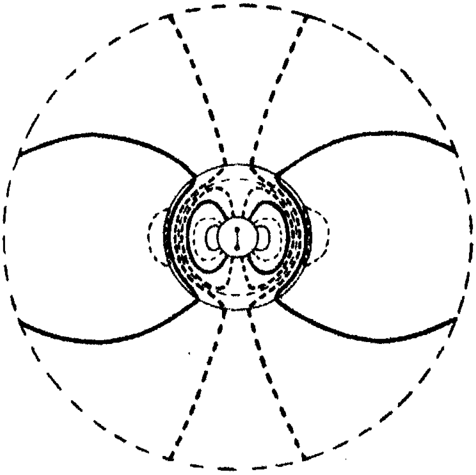
$$\Theta = \frac{A}{r^3}\sin\frac{2\pi\epsilon}{\lambda},$$

FIG. 4.



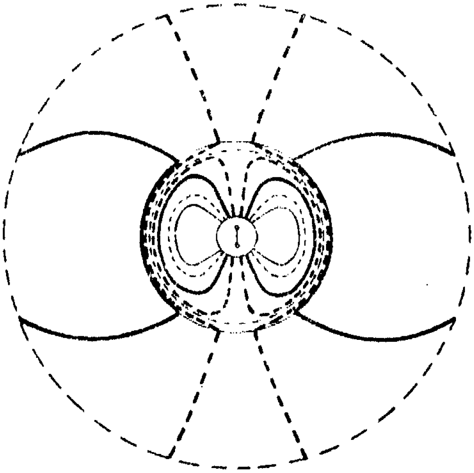
$t = (0{\cdot}26)\,2\tau$.

FIG. 5.



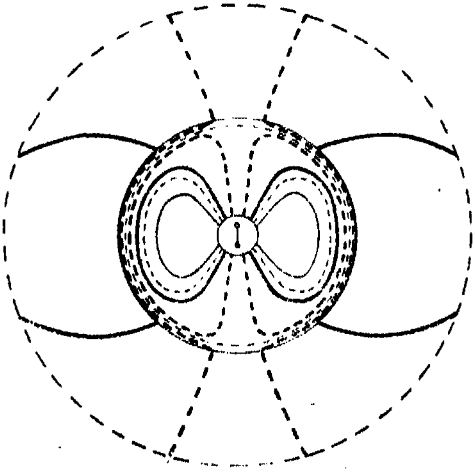
$t = (0{\cdot}385)\,2\tau$.

Fig. 6.



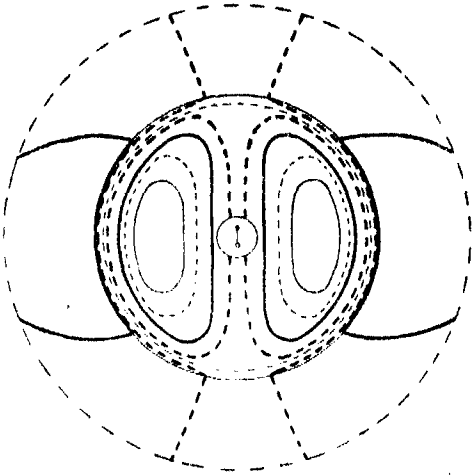
$t = (0{\cdot}51)\,2\tau.$

Fig. 7.



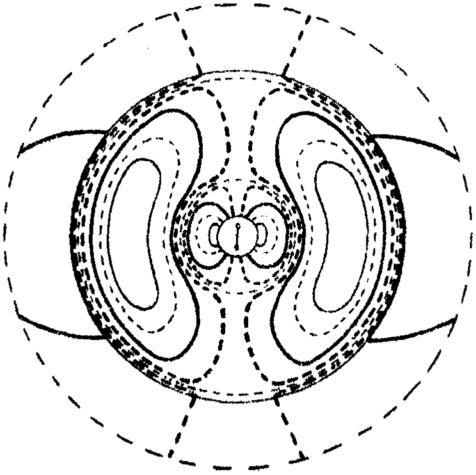
$t = (0{\cdot}635)\,2\tau.$

Fig. 8.



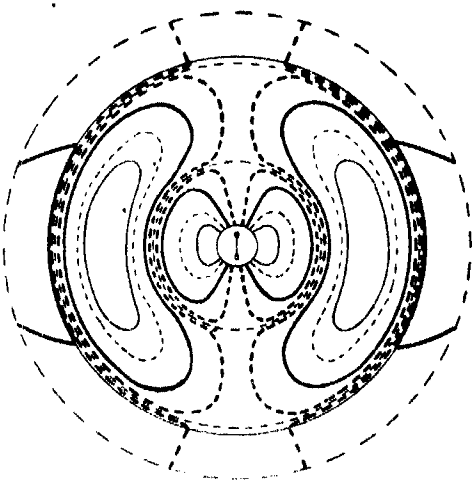
$t = (0{\cdot}76)\,2\tau.$

Fig. 9.



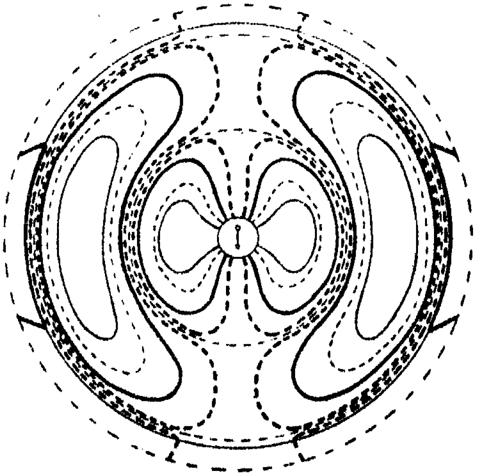
$t = (0{\cdot}885)\,2\tau.$

FIG. 10.



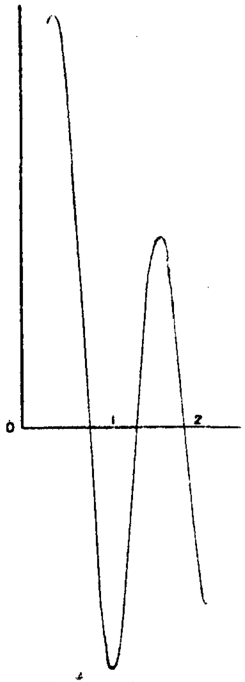
$t = (1\cdot01)\, 2\tau$.

FIG. 11.



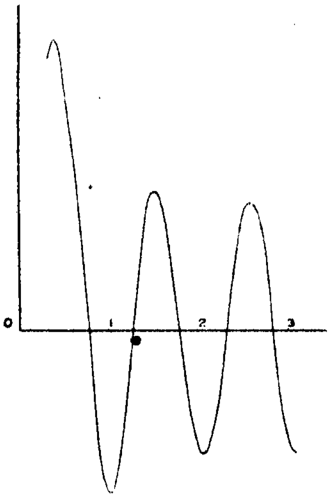
$t = (1\cdot185)\, 2\tau$.

FIG. 1



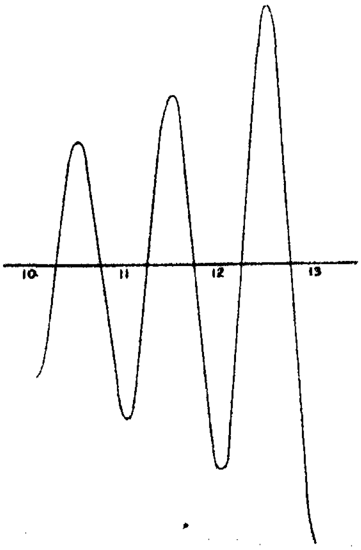
Front of waves after two periods.

FIG. 2.



Front of waves after three periods.

FIG. 3.



Front of waves after thirteen periods.

when $ct<r$. Figs. 1—3 of Plate 6, represent parts of the curves, of which Θ is ordinate and r is abscissa, at instants which are the ends of the second, third, and thirteenth periods from the beginning of the vibrations.* The parts of the curves in figs. 1 and 2, which are very near the oscillator, are omitted, and, in the three curves, the parts which lie beyond the advancing wave-fronts are indistinguishable from the axis of abscissæ. In figs. 1 and 2, as originally drawn, A was given the value 0·1, and ν and ϵ have the same values as in the previous discussion. In fig. 3 A was given the value 1. The curve in fig. 3 has been drawn for values of r between $r = 10\lambda$ and $r = 13\lambda$. In each case the terminal point of the curve towards the right represents the value of Θ at the advancing wave-front at the instant in question. Near the oscillator, the maxima and minima values of Θ diminish as the distance of them from the oscillator increases, as is shown in figs. 1 and 2. This is due to the preponderance of the factor $1/r^3$ when r is small. When the front of the train of waves has travelled over as few as three wave-lengths, this tendency is already checked by the tendency of the factor $e^{\nu r/\lambda}$ to increase with r, as is seen in fig. 2, where the last minimum is almost exactly equal to the previous maximum. When the front of the train of waves has travelled over a larger number of wave-lengths, the maxima and minima near the front exceed those at a little distance behind the front, as is shown in fig. 3, where there is a regular increase in the maxima and minima values as the front of the train of waves is approached. A comparison of figs. 1 and 2 with each other shows the diminution of the maxima and minima at the same places as time goes on. This is due to the damping of the oscillations by radiation. The same comparison shows also that the maxima and minima near the front of the train of waves do not suffer diminution to the same extent, and the same thing is shown by comparing fig. 3 with these, allowance being made for the difference of scale. In fact, the disturbance at the front of the wave-train suffers diminution through spherical divergence only, for the factor $e^{-\nu(ct-r)/\lambda}$ has the value unity at the front of the waves, and, when r is at all large, the value of Θ at the front is very nearly equal to

$$-A \sin(2\pi\epsilon/\lambda)(4\pi^2+\nu^2)/\lambda^2 r,$$

so that it is very nearly proportional to r^{-1}.

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* In the arithmetical work which is requisite for tracing these curves and in some of the remaining arithmetical work of the paper, I had the good fortune to secure the collaboration of Mr. J. W. Sharpe, formerly Fellow of Gonville and Caius College, Cambridge, who made the necessary calculations. The paper is much more complete than it would have been without his help.

"On Flame Spectra." By CHARLES DE WATTEVILLE. Communicated by ARTHUR SCHUSTER, F.R.S. Received May 28,—Read June 16, 1904.

(Abstract.)

In order to obtain the spectrum of any substance, it has generally been considered sufficient to introduce a small quantity of it into an already formed flame. In the course of a photometrical investigation of flames which had been coloured by injecting the spray from saline solutions into the gas to be burnt, M. Gouy discovered in the spectra of the flames several new lines belonging to the metal contained in the solution.* Instead of appearing throughout the whole flame, as did the previously known lines, these new lines were only emitted in the vicinity of the inner blue cone—the origin of the Swan spectrum. The observations of M. Gouy were limited to the examination of certain lines of the visible portion of the spectrum, and, with the advice of Professor Schuster, and under his direction, I have taken up this study with the object of extending it, by means of photography, to the ultra-violet portion of the flame, and also of detecting lines which are too feeble to be visible to the eye.

The method employed for the production of the flame is, in short, that which has been introduced by M. Gouy, and described by him in his memoir, to which reference should be made for a description. The very slight modifications which have been made in the apparatus of this scientist are due to the necessity of having an arrangement which should be as automatic as possible during the 8 hours which were often found necessary for the photographic exposures. These modifications, however, have an important bearing upon the success of the experiments.

The spectroscopical apparatus used has been of two kinds—a fine Rowland concave grating of 1-metre radius and prism spectroscopes. The results obtained by means of the grating have been completed, as regards the very weak lines, with the help of the prism spectroscope.

The lines in the spectra obtained under the conditions of my experiments are very much more numerous than is the case when all the portions of the flame do not participate in the production of the phenomena. Not only are all the lines present which were seen by Professor Hartley in the oxy-hydrogen blowpipe flame, but, in addition, there are a large number of other lines which only extend to the height of the blue inner cone. Moreover, the flame spectra extend sufficiently far into the ultra-violet in order to enable the line 2194 of tin to be observed.

If we compare the flame spectra thus produced with those of the arc and the spark, it will be noticed that, as a rule, the lines which are

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* 'Annales de Chimie et de Physique,' 5th Series, vol. 18, 1879.

found in the flame spectrum are those which are the strongest lines in the arc spectrum. In certain cases, some of the more intense arc lines are absent, whereas less intense arc lines are to be found in the flame spectrum. On the other hand, none of the characteristic lines of the spark spectrum are ever seen in the flame spectrum. The resemblance, however, is very marked between the flame spectrum and that of the spark which has been made oscillatory by the introduction of a self-induction into the discharging circuit of a condenser. In the latter case, as is well known from the work of Dr. Hemsalech, the spark spectrum is considerably simplified.* Moreover, although the flame spectrum will contain only the lines which belong to the spectrum of the oscillatory spark, yet all the lines of the latter will not be found in the flame spectrum, the missing lines being those which are peculiar to the ordinary spark spectrum, and which only exist in the immediate neighbourhood of the electrodes, becoming shorter and shorter, and finally disappearing as the self-induction is increased.

The preceding paragraph refers to metals other than those belonging to the iron group. On the contrary, there is a most striking similarity between the flame spectra of iron, of nickel, and of cobalt, and the oscillatory spark spectra of the same metals in the region included between about 4300 and 2700 Ångström units. The similarity of the two spectra is so great that, except for very small differences of intensity, the oscillatory spark spectrum, which is photographed as a comparison spectrum in the centre of the flame spectrum, appears to be a prolongation of the latter. It should be noticed that if in the visible portion of the spectrum certain lines appear to be missing, it is doubtless because the continuous spectrum prevents these feeble lines from being seen. This explains why M. Gouy was not able to observe the nickel lines which are found on the photographs taken with various salts of nickel, viz., the sulphate, chloride, and ammoniacal chloride. In the ultra-violet the spectrum of the flame appears to fade away a little more rapidly than that of the oscillatory spark, but it is probable that this difference would be reduced by prolonging the time of exposure; since it is, of course, the radiations of the shortest wave-length which are most absorbed by different media.

It is very probable that the reason for this similarity between the spectrum of the flame and the spectrum of the oscillatory spark is entirely a question of temperature. On the one hand, the increase in the number of lines of the flame spectrum obtained by the use of the sprayer may be attributed to the fact that the hottest regions of the flame take part in the production of the phenomena, and, on the other hand, the diminution in the number of lines in the spark spectrum when the spark becomes oscillatory is due to a diminution of its temperature.

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* 'Sur les Spectres d'Etincelles.' Paris, Hermann.

[D 7200, 0550 – Oϵ].

"The Retardation of Combustion by Oxygen." By HENRY E. ARMSTRONG, Ph.D., F.R.S.

Received June 9,—Read June 16, 1904.

In the course of his researches on gaseous explosions, H. B. Dixon has laid stress on the fact that carbon monoxide, rather than the dioxide, is the initial product of the combustion of carbon and of its gaseous compounds; moreover, he has shown that water plays a peculiar and all-important part in the combustion of the monoxide; and he has proved, in a number of cases, that oxygen is by far the most effective diluent in retarding combustion. These, in some respects, paradoxical conclusions have not yet been sufficiently explained. Recent researches[*] emanating from the Manchester school have brought new facts to light, however, which have an important bearing on the interpretation of explosive changes—so much so, indeed, that it is no longer difficult to paint a consistent and fairly complete picture of the mechanism of combustion.[†]

1. It would seem that, in the case of hydrocarbons, there is no preferential combustion either of hydrogen or of carbon: initially, the hydrocarbon merely undergoes *hydroxylation*. As hydroxylation proceeds more readily when it has once taken place—owing to the attraction of oxygen for oxygen—the first product may easily escape observation: thus, Bone and Wheeler were unable to detect the formation of hydroxymethane (methyl alcohol) from methane; Bone and Stockings, however, succeeded in obtaining ethyl alcohol, C_2H_5OH, from ethane, C_2H_6.

2. A stage in the hydroxylation is soon reached when *thermoschisms* begin to take place. Thus, dihydroxymethane breaks up as soon as it is formed into water and formaldehyde, which is in turn easily resolved into hydrogen and carbon monoxide:

$$CH_2(OH)_2. \longrightarrow CH_2O + OH_2 \longrightarrow CO + H_2 + OH_2.$$

Dihydroxyethane, in like manner, gives rise to acetaldehyde, which, under some conditions, breaks up into methane and carbon monoxide:

$$C_2H_4(OH)_2 \longrightarrow CH_3.COH + OH_2 \longrightarrow CH_4 + CO + OH_2.$$

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[*] W. A. Bone and R. V. Wheeler, "The Slow Oxidation of Methane at Low Temperatures," 'Chem. Soc. Trans.,' 1902, vol. 81, p. 536; 1903, vol. 83, p. 1074. W. A. Bone and W. E. Stockings, "The Slow Combustion of Ethane," *ibid.*, 1904, vol. 85, p. 693.

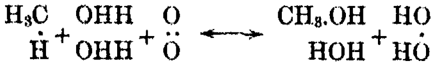
[†] Compare H. E. Armstrong, "The Mechanism of Combustion," *ibid.*, 1903, vol. 83, p. 1088.

3. It is to be supposed that the more complex hydrocarbons are, to a large extent, resolved into simpler thermoschists prior to oxidation, *e.g.*,

$$C_6H_{14} \longrightarrow C_3H_8 + C_3H_6\,;\; C_2H_6 \longrightarrow C_2H_4 + H_2.$$

The change may extend even to the formation of carbon, when a relatively small proportion of oxygen is present. In high temperature changes (explosions), such thermoschisms probably play an all-important part.

4. The precise manner in which oxygen is introduced into the hydrocarbon molecule is a matter of some interest. If oxygen molecules were directly active as wholes and the actual, immediate and sole cause of the oxidation, there would seem to be no reason why the dihydroxy-derivative should not be directly produced rather than the monhydroxy: the observation made by Bone and Stockings, that ethyl alcohol is producible from ethane, therefore, is of crucial importance. But, on general grounds, regarding the change as electrolytic in character, it is probable that the electrolyte, *i.e.*, conducting water, is the immediate source of the oxygen; and that the oxygen molecule* plays the part of depolariser. From the same point of view, it appears probable that the water molecules contribute hydroxyl rather than oxygen. The process may be formulated as involving the conjugation of hydrocarbon (probably through its carbon) with water (acting primarily as the catalyst or associating agent) and oxygen, thus:



$$\begin{array}{c}H_3C\\ \dot{H}\end{array} + \begin{array}{c}OHH\\ OHH\end{array} + \begin{array}{c}O\\ \ddot{O}\end{array} \longleftrightarrow \begin{array}{c}CH_3.OH\\ HOH\end{array} + \begin{array}{c}HO\\ \dot{HO}\end{array}$$

5. According to the view here advocated, carbon dioxide is necessarily a later product of change than the monoxide—in fact, the final product. It is to be supposed that, in its formation from the monoxide, the latter is first converted into formic acid. On this assumption, it is easy to understand that the presence of so large a proportion of water is required in order that the explosive wave may attain to its greatest velocity, as the affinity of water for carbon monoxide is relatively slight and the reversible change one which takes place mainly in the direction:

$$HCO(OH) \longrightarrow CO + OH_2.$$

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* The need of distinctive names for oxygen-stuff or atomic oxygen and of the molecular oxygen we handle is very obvious in discussing such a point as this.

The figures given by Dixon are as follows:—[*]

Condition of mixture.	Per cent. of steam present.	Mean rate in metres per second.
Well dried	...	1264
Dried	...	1305
Saturated at 10° C.	1·2	1676
" 20	2·3	1703
" 28	3·7	1713
" 35	5·6	1738
" 45	9·5	1693
" 55	15·6	1666
" 65	24·9	1526
" 75	38·4	1266

The gradual retardation observed when the proportion of steam is increased beyond 5·6 per cent. may be due to a variety of causes: to the steam acting as a diluent; to an increase in the extent to which water is unburnt by the carbon monoxide; and, perhaps, in no slight measure, also to the tendency of the steam to hold back the oxygen.

6. It is to this last circumstance that the marked influence of oxygen in retarding combustion is probably attributable. This influence is especially noteworthy in the case of electrolytic gas, inasmuch as excess of hydrogen has precisely the opposite effect and nitrogen retards the explosion less than does an excess of oxygen. According to Dixon, the rates, in metres per second, at which various mixtures of hydrogen and oxygen and of electrolytic gas and nitrogen explode, are as follows:—

$4H_2 : \frac{1}{2}O_2$	3532		
$3H_2 : \frac{1}{2}O_2$	3527		
$2H_2 : \frac{1}{2}O_2$	3268		
$H_2 : \frac{1}{2}O_2$	2821		
$H_2 : O_2$	2328	$H_2 : \frac{1}{2}O_2 + \frac{1}{2}N_2$	2426
$H_2 : 2O_2$	1927	$H_2 : \frac{1}{2}O_2 + 1\frac{1}{2}N_2$	2055
$H_2 : 3O_2$	1707	$H_2 : \frac{1}{2}O_2 + 2\frac{1}{2}N_2$	1822
$H_2 : 4O_2$	1281		

In seeking for an explanation of this remarkable, if not paradoxical, behaviour of hydrogen, it is necessary to remember that, whereas both oxygen and water molecules diminish in stability as the temperature rises, the stability of hydrogen peroxide must be at a maximum at a high temperature[†]—since its formation from oxygen and water is an endothermic process. In fact, it is to be supposed that water is readily oxidised at temperatures such as prevail in combustions. If, however, the formation of water be regarded as involving the changes

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[*] 'Phil. Trans.,' A, 1893, vol. 184, p. 97.

[†] Nernst, 'Zeit. physikal Chem.,' 1903, vol. 46, p. 720, has endeavoured to deduce numerical estimates of the stability of hydrogen peroxide at high temperatures; the results arrived at, however, are not satisfactory owing to the paucity of data.

$$\begin{array}{c}\mathrm{H}\\ \cdot\\ \mathrm{H}\end{array} + \begin{array}{c}\mathrm{OHH}\\ \\ \mathrm{OHH}\end{array} + \begin{array}{c}\mathrm{O}\\ \cdot\cdot\\ \mathrm{O}\end{array} \longleftrightarrow \begin{array}{c}\mathrm{HOH}\\ \\ \mathrm{HOH}\end{array} + \begin{array}{r}\mathrm{HO}\\ \cdot\\ \mathrm{HO}\end{array}$$

$$2H_2O_2 \longleftrightarrow 2H_2O + O_2$$

it follows that water and oxygen will mutually hold each other in check: so that when electrolytic gas is exploded there will be a deficiency of oxygen, as it were, owing to its conversion into hydrogen peroxide, which may be regarded as relatively, if not entirely, inoperative as an oxidising agent at high temperatures in presence of oxygen. On the other hand, when excess of oxygen is present, the water—which is the effective catalyst—will be more or less held back, also in consequence of its oxidation to hydrogen peroxide. The marked influence of hydrogen in promoting the combustion of electrolytic gas is in full harmony with this conclusion; indeed, it is difficult to explain it in any other way than by supposing that, when present in excess, the hydrogen serves to promote the dissociation of the peroxide by diminishing the proportion of active oxygen present: in other words, according as hydrogen or oxygen is in excess, equilibrium is disturbed in one direction or the other. The interaction of hydrogen and oxygen may, perhaps, be supposed to be incomplete at high temperatures, less because the steam is partially dissociated than on account of the division of the oxygen between the hydrogen and water.

[*Note added June* 29.—The experiments on the oxidation of ethane at so low a temperature as 300, recently described by Bone and Stockings, have shown that change proceeds with surprising rapidity in the case of mixtures containing ethane and oxygen in the ratio 2 : 1 or 1 : 1, the oxygen disappearing within 30—45 minutes; whereas when sufficient oxygen was present to burn the hydrocarbon completely to steam and carbon dioxide (1 : 3·5), a considerable quantity of oxygen and some ethane remained unchanged even after 2 days. There can be little doubt, therefore, that oxygen has a specific retarding effect even at so low a temperature as 300°; and there would seem to be no reason to suppose that the changes which occur at low temperatures are in any essential respect different from those at high temperatures.]

"A Probable Cause of the Yearly Variation of Magnetic Storms and Auroræ." By Sir NORMAN LOCKYER, K.C.B., LL.D., F.R.S., and WILLIAM J. S. LOCKYER, M.A. (Camb.), Ph.D. (Gött.), F.R.A.S., Chief Assistant Solar Physics Observatory. Received June 3,—Read June 16, 1904.

The ordinary meteorological elements, such as atmospheric pressure, temperature, etc., have a yearly change satisfactorily explained as due to changes of the position of the earth's axis in relation to the sun, or, in other words, the variation of the sun's declination. There are, however, other phenomena, such as magnetic disturbances and auroræ, which have been explained differently.

Thus, in regard to this seasonal variation Mr. Ellis* has written, "The related physical circumstance is that at the equinoxes, when disturbance is more frequent, the whole surface of the earth comes under the influence of the sun, whilst at the solstices, when magnetic disturbance is less frequent, a portion of the surface remains for a considerable period in shadow."

The object of the present communication is to put forward another possible cause.

It has been previously pointed out† that a very close relationship exists between the epochs of occurrence of prominences in the polar regions of the sun and Ellis's "great" magnetic disturbances. This synchronism showed that either the polar prominences themselves, or the disturbances thus indicated in these polar regions, were the origin of these "great" magnetic storms, or that they were caused by a more general stirring-up of a greater extent in latitude of the solar atmosphere.

A further investigation‡ indicated, however, that in all probability it was either the actual polar prominences themselves, or the activity in the solar polar regions, that initiated these magnetic disturbances, for it was there pointed out that the presence of polar prominence activity-tracks synchronised with the appearances of large "polar" coronal streamers. Here we have an indication of a local cause and effect.

It will be gathered, then, that, even as regards terrestrial magnetic phenomena, considerable importance must be attached to action taking place in the regions about the solar poles.

Since the axis on which the sun rotates is inclined to the plane of the ecliptic, there will be times throughout the course of a year when the solar polar regions will be exposed most and least to the earth.

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* 'Monthly Notices,' vol. 61, p. 540.

† 'Roy. Soc. Proc.,' vol. 71, p. 244; also 'Monthly Notices, R.A.S.,' vol. 63, Appendix I, p. 6.

‡ 'Monthly Notices, R.A.S.,' vol. 63, p. 481.

It should be expected, then, that if the polar regions of the sun have any action, as above suggested, the effects of the action on the earth should vary according to the positions of the solar poles relative to the earth.

The actual inclination of the sun's axis being 82° 45′, and the longitude of the ascending node being 74° 25′, or the tilt of the axis being in the direction of about 19 hours in right ascension, it follows that, in each year, the south pole of the sun is most turned towards the earth in the beginning of March (about the 6th), and the north pole most towards the earth in the beginning of September (about the 5th). At the two intermediate epochs, in June (about 5th) and December (about 6th), neither pole is turned towards or away from the earth, but occupies an intermediate position. Hence we see that the equinoxes occur in the same months as those in which one or other of the solar poles is turned towards the earth, while the neutral positions of the solar poles in relation to the earth occur in the same months as the solstices.

The accompanying diagram shows graphically the relation between the two curves representing the variation of the sun's declination and the change of the latitude of the sun's centre or the variation of the amount of the tilt of the solar poles, in relation to the earth throughout a year.

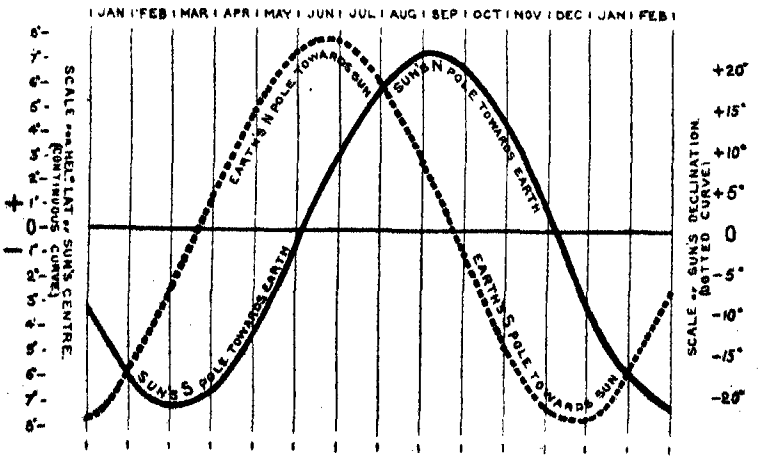

Fig. 1.—Curves showing the relation between the change of declination of the Sun (broken curve) and the positions of the Sun's north and south poles with regard to the earth (continuous curve) throughout a year.

It will be seen that the curve representing the tilt of the solar axis is nearly (a little less than) a quarter of a phase in advance of that indicating the declination change, so that the maximum or minimum point of the latter curve is only slightly in advance of the *mean* points respectively of the former curve.

If, therefore, these solar polar regions are capable of disturbing the magnetic and electric conditions on the earth, as has been above suggested, then, when they are most directed to her at the equinoxes, the greatest effects during a year should be recorded, and when they are least directed the effects should be at a minimum.

It will not be necessary here to refer at any great length to statistics relating to the annual inequality of magnetic disturbances and auroræ, for these have been very efficiently worked out and the results published by Mr. William Ellis.*

Mr. Ellis has shown that the curves of frequency of magnetic disturbances at Greenwich and Paris are very similar, "showing maxima at or near the equinoxes, and minima at or near the solstices." These also, he further points out, are similar, with regard to the epochs of maxima, to the curve representing the frequency of the aurora at London. In the case of auroræ observed in Edinburgh, North-East Scotland and in different regions in Scandinavia, the months in which the greatest frequency is recorded are September and October (perhaps more generally October) and March and April (perhaps more generally March). Mr. Ellis is inclined to the opinion that there is a small tendency for the autumn maximum to become a little later (from September to October) and the spring maximum somewhat earlier (from April to March) as higher latitudes are approached.

Further, he points out that in more northern latitudes the mid-winter minimum of lower latitudes appears to diminish and eventually disappears, so that the curve of frequency of the aurora between October and March is practically flat with a small intermediate maximum about January. This change in form of the frequency curve in regions in close proximity to the magnetic pole, and where the conditions of day and night are so different, is of great interest, but requires careful consideration before it can be regarded as representing real auroral changes.

The accompanying curves, fig. 2, illustrate the relation throughout a year between the positions of the earth's poles with reference to the sun; the positions of the sun's poles as regards the earth; the frequency of magnetic storms at Greenwich and Paris; and lastly, the frequency of the aurora as observed at Edinburgh and at stations in Scandinavia below latitude 65° N. The first two curves are those that have already been given in fig. 1, but plotted differently. They have here been so arranged that the maxima points represent the epochs when each of the poles is most inclined to the sun or earth as the case may be. Both the magnetic and auroral curves represent four of the set of curves which Mr. Ellis* has recently published.

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* 'Monthly Notices, R.A.S.,' vol. 60, p. 142; vol. 61, p. 537; vol. 64, p. 229.

It need scarcely be pointed out that the low minima of the auroral curves during the summer months are due in great part to the shortness of the nights, and therefore to the restriction of the time available for aurora observations.

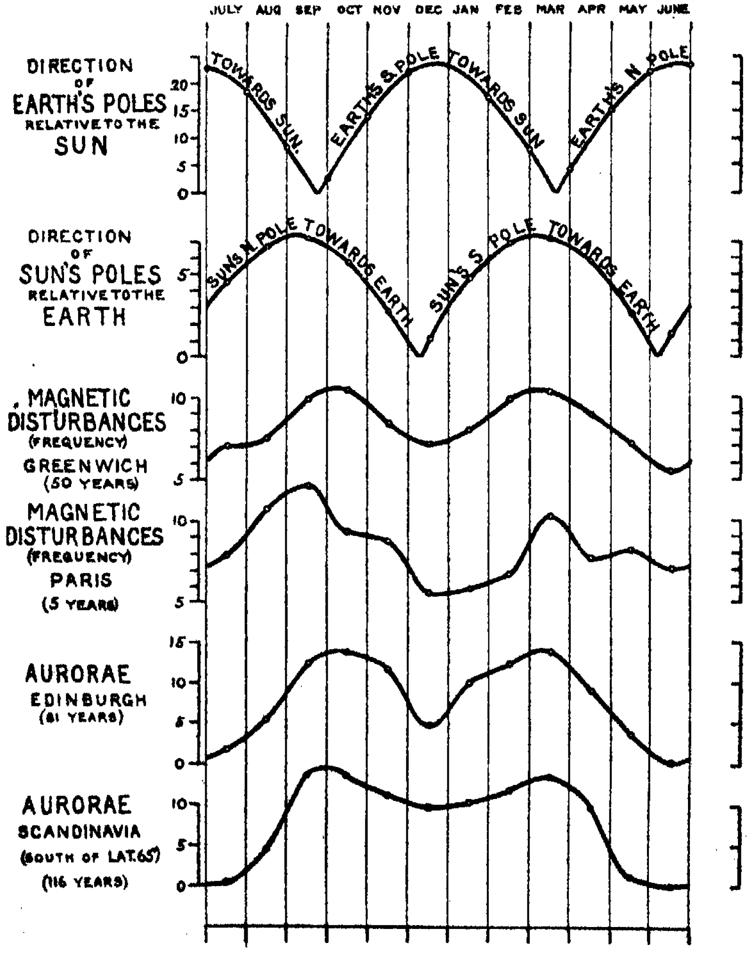

FIG. 2.—Curves showing the relationship between the positions of the Sun's north and south poles with regard to the earth and the frequency of magnetic disturbances and auroræ throughout a year.

The coincidence in time between the epochs of the maxima of the frequency of magnetic disturbances and auroræ, and those of the greatest inclination towards the earth of the north and south solar polar regions is clearly indicated.

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* 'Monthly Notices, R.A.S.,' vol. 64, p. 229.

It is interesting to inquire in what way this yearly inequality of terrestrial magnetic phenomena is influenced when the sun's polar regions are, for different groups of years, in an undisturbed and disturbed condition.

It would be expected that the oscillation of more disturbed solar polar regions towards and away from the earth would tend to *increase the difference* between the frequency of magnetic disturbance at the equinoxes and solstices, while this difference for those years when the less disturbed solar polar regions are in action, should be somewhat *reduced.* That this is actually the case is brought out by the figures which Mr. Ellis has given in the publication of which mention has already been made.

Since the greatest magnetic storms are closely associated in point of time with prominence disturbances in the polar regions of the sun, to make the necessary comparison, therefore, the years in which "great" magnetic storms occurred should be grouped together and the yearly inequality determined, and another group of years in which "great" magnetic storms were less frequent formed and the yearly inequality also determined. Fortunately a computation already made can be utilised for this comparison, for Mr. Ellis has determined the number of days of greater frequency (near sunspot maximum), and lesser frequency (near sunspot minimum), of magnetic disturbance, both groups practically including the conditions required. Thus he has formed groups of the years 1848—51, 1858—61, 1869—72, 1882—85, 1892—95, which include, at any rate for the last three groups, the years where prominences were in high latitudes and another series of groups of years, 1854—57, 1865—68, 1876—79, 1887—90, which are years when prominences were less frequent in those regions.*

The interesting conclusion to which Mr. Ellis arrived was that "the excess of the equinoctial frequency over the solstitial frequency is greater, the greater the degree of disturbance."

This result thus helps to endorse the suggestion made in a previous paragraph that the greater the disturbed solar polar regions, the greater the difference between the magnetic frequency at the equinoxes and solstices.

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* The fact that continuous observation of solar praminences was only commenced in 1870 accounts for our lack of knowledge of the frequency of this class of phenomena before that date. Since, however, during the last three sunspot cycles it has been observed that polar prominences are most frequent just a little after a sunspot minimum and up to and at the epoch of the following sunspot maximum, it may be concluded that their appearance previous to the year 1870 occurred at the same times in relation to the sunspot cycle. Ellis's groups of years previous to that date, namely, 1848—51 and 1858—61, may on these grounds be classed as years in which polar prominences were present, whilst the groups 1854—57 and 1865—68 may be taken as epochs when polar prominences were not so frequent.

Conclusions.

The conclusions arrived at in the above paper may be briefly stated as follows :—

1. The seasonal variation in the frequency of magnetic storms and auroræ depends on the positions of the sun's axis in relation to the earth.
2. The epochs of the greatest inclinations of the sun's axis towards or away from the earth, or in other words the greatest exposure of the N. or S. solar polar regions to the earth during a year, correspond to those of greatest magnetic and auroral frequency.
3. The epochs (groups of years), when the solar polar regions are most disturbed, synchronise with those when the excess of the equinoctial over the solstitial frequency of magnetic storms is greatest.

"The Fossil Flora of the Culm Measures of North-west Devon, and the Palæobotanical Evidence with regard to the Age of the Beds."

By E. A. NEWELL ARBER, M.A., F.L.S., F.G.S., Trinity College, Cambridge, University Demonstrator in Palæobotany. Communicated by Professor MCKENNY HUGHES, F.R.S.

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(Abstract.)

The carboniferous rocks which occupy an area of 1200 square miles in Devon, Somerset, and Cornwall, are generally known as the Culm Measures, a name first applied to them by Sedgwick and Murchison in 1838; the word "culm" being an ancient Devonshire term for the impure coal, which is confined to one horizon in these beds in the neighbourhood of Bideford.

Sedgwick and Murchison, in their classic memoir on the physical structure of Devonshire (1840), instituted a twofold division of these rocks, the Upper and the Lower Culm Measures, and this classification is maintained here. At the present time, our knowledge of the Lower Culm Measures is on an altogether different footing to any which we possess of the Upper division. This is largely due to the work of Messrs. Hinde and Fox (1895), who showed that this division is of Lower Carboniferous age. The Upper Culm Measures, which form by far the greater thickness of the Devonshire carboniferous rocks, are, however, of Upper Carboniferous age. This was first proved by De la Beche (1838), on the evidence of the plant remains of the beds

near Bideford, and this conclusion was confirmed and maintained by Sedgwick and Murchison.

The present paper is an attempt to extend our knowledge of the distribution of Carboniferous plants in Devonshire, and also to determine the horizons in the Upper Carboniferous, which are represented by the Upper Culm Measures.

The task of the collection of well-preserved plant remains from these rocks has been exceedingly difficult, partly on account of the severe crushing and folding which the strata have undergone, and partly because, with one exception, the coal or culm is no longer worked in the district. The best-preserved impressions are only found in close association with the culm, and, at the present time, few traces of former culm workings remain, and these are fast disappearing. Thus, the specimens described here, are in some respects unique, and, in many cases, only a single example of the species is known.

The coal or "culm" forms a number of inconstant bands of no great thickness, which run from the western coast-line through Bideford for a distance of 12 miles to the east, near Chittlehampton. These bands are practically confined to one horizon, and this is one of the very few horizons which can be recognised in the great series of the sandstones and shales of the Upper Culm Measures by its lithological character. In the present paper, attention has been confined to the flora of these beds.

Several species of plant remains have been already recorded by De la Beche, Sedgwick and Murchison, and T. M. Hall, and, of most of these, further specimens have been collected, and, in addition, many records new to Devonshire have been made. Among the latter may be mentioned the first British record of *Neuropteris Schlehani*, Stur, a frond of common occurrence in the Coal Measures of the Continent, and a leaf new to Britain, which somewhat recalls Dawson's genus, *Megalopteris*, chiefly known from the Coal Measures of Canada and the United States.

Determinations from the Bideford District.

Equisetales.

- *Calamites* (*Calamitina*) *undulatus*, Sternb.
- *Calamites* (*Eucalamites*) *ramosus*, Artis.
- *Calamites* (*Stylocalamites*) *Suckowi*, Brong.
- *Calamites* (*Calamitina*) *varians*, Sternb.
- *Calamites* sp. (external surface).
- *Annularia radiata*, Brong.
- *Annularia galioides* (L. and H.).
- *Calamocladus equisetiformis* (Schl.).
- *Calamocladus charæformis* (Sternb.).
- *Calamostachys longifolia* (Weiss).
- *Pinnularia* sp.

Sphenophyllales.
  Sphenophyllum cuneifolium (Sternb.).
Cycadofilices.
  Neuropteris obliqua (Brong.).
  Neuropteris Schlehani, Stur.
  Alethopteris Serli (Brong.).
  Alethopteris lonchitica (Schl.).
Filicales (?).
  Mariopteris muricata (Schl.).
  Urnatopteris tenella (Brong.).
  Renaultia footneri (Marrat).
  Renaultia schatzlarensis (Stur) (?).
  Megalopteris (?) sp.
Lycopodiales.
  Lepidodendron aculeatum, Sternb.
  Lepidodendron obovatum, Sternb.
  Lepidodendron fusiforme, Corda.
  Lepidophloios acerosus (L. and H.).
  Sigillaria scutellata, Brong.
  Sigillaria tessellata, Brong.
  Stigmaria ficoides (Sternb.).
Cordaitales.
  Cordaites (*Artisia*) sp.
Incertæ sedis.
  Trigonocarpus Parkinsoni, Brong.

The opinions which have been held with regard to the age of the Upper Culm Measures of Devon, and the horizons which they represent, may be briefly summarised as follows:—De la Beche, and Sedgwick and Murchison regarded these beds, as has been already stated, as the equivalents of the Upper Carboniferous in other British Coal-fields, and by the year 1840 this conclusion was generally accepted. There appears to have been some doubt, however, in more recent times as to the exact subdivision of this great series to which the Bideford beds should be referred. Townshend Hall (1866—1878) regarded them, on lithological grounds, as the equivalents of the Millstone Grit. Pengelly (1867), and Murchison (1872) referred them to the Coal Measures, and Mr. H. B. Woodward (1887) doubtfully to the Lower Coal Measures. Mr. Ussher (1888—1901) has not expressed any decided views on this subject; he appears to be inclined to support Hall's view that these beds are equivalent to the Millstone Grit in other areas.

We see, therefore, that previous conclusions, based on grounds other than palæontological, have apparently not been put forward with much confidence.

It may be also noticed that there would seem to be a tendency at the present time in certain quarters to regard the Culm Measures as essentially a Lower Carboniferous series of deposits. Professor Hull's* (1881) opinion that "the flora of the 'culm'" belongs "to the Lower Carboniferous series of Devonshire" is a case in point. This view is not, however, shared by all British geologists. It has arisen partly from the fact that the older literature has to some extent been lost sight of, and partly from the great interest aroused by the work of Messrs. Hinde and Fox, which has brought into special prominence that portion of the Culm Measures which is of Lower Carboniferous age. We have also in recent years gained a more intimate acquaintance with the flora of the so-called "culm" or "kulm" of Germany, Austria, and elsewhere on the Continent; deposits of Lower Carboniferous age, as shown by the character of their fossil remains.

In recent years we have come to know more of the distribution of fossil plants in the Coal Measures of this country, chiefly as the result of Mr. Kidston's researches, and it is now possible to distinguish clearly a certain number of horizons in the Upper Carboniferous. During Upper Carboniferous and Permian times, periods which belong to the same botanical epoch, the general character of the flora in its broad outlines remained constant. Yet detailed study has shown that it is possible to detect the gradual changes which took place during this interval, and the underlying principle of zoning the Carboniferous system depends upon the recognition of definite periods in which these changes became more marked. Thus the general character of the flora of the Bideford district is identical with that found elsewhere in Britain in *Middle Coal Measure* times. The majority of the species recorded here are known to occur in both the Middle and Lower Coal Measures. But there are also others, such as *Alethopteris Serli*, and *Calamocladus charæformis*, which are unknown from the Lower Coal Measures, and others again, such as *Sigillaria tessellata* and *Neuropteris obliqua*, which are markedly more abundant in the Middle than the Lower Coal Measures. In other words, the change in the general character of the flora of the Upper Carboniferous, as traced from the base to the summit, is already marked on this horizon by the presence of species which are not found in the lower beds. On the other hand, there is an entire absence of certain genera and species, especially of the genus *Pecopteris*, which are characteristic in this country of higher horizons such as the Upper Coal Measures. Thus *the horizon in the Upper Carboniferous represented by that portion of the Upper Culm Measures in which the coal or culm occurs in the Bideford district is equivalent to the Middle Coal Measures in other*

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* 'Coal Fields of Great Britain,' 4th edit., p. 64.

British coal-fields; a higher horizon than has so far been assigned to these beds.

There is also evidence of a different nature which points to the conclusion that the Lower Coal Measures are also represented in Devon. In beds at Instow, some 2½ miles to the north of Bideford, which are admitted to occupy a lower horizon than those at Bideford, fish and Goniatite remains have been recorded by the late Townshend Hall (1876). The fish remains are estuarine, and belong to the following species:—

Cœlacanthus elegans, Newb.
Elonichthys aitkeni, Traq.

The Goniatites are as follows:—

Gastrioceras carbonarium (von Buch).
Gastrioceras Listeri (Martin).

Most of these species are, I believe, characteristic of the Lower Coal Measures, although not confined to that horizon.

With regard to the higher beds of the Culm Measures—the Eggesford Grits in Mr. Ussher's classification—there is no evidence of horizon at present, but it is hoped that the examination of these rocks which is shortly to be undertaken will be successful in solving this problem by means of the plant remains which are known to occur in this series.

Lastly it may be pointed out that the use of the term "culm" or "kulm," with regard to certain series of deposits in Germany and Austria, is particularly unfortunate, for these beds are entirely of Lower Carboniferous age, as is shown by the character of their plant remains, now well known from the researches of Stur, Göppert, Potonié, and others. Although Lower Carboniferous rocks of great interest occur in Devon and the adjacent counties, they form only a small fraction of the thickness of the Culm Measures which, as a whole, are essentially Upper, and not Lower Carboniferous in age, and to which, in part at least, the ordinary nomenclature applied to other British coal-fields has been shown here to be applicable.

I am under great obligations to many geologists for assistance during the course of this work, obligations which will be acknowledged at length in the paper. I cannot refrain, however, from expressing my great indebtedness to Mr. Inkermann Rogers, of Bideford, for the time and patience which he has devoted to the collection of plant remains with a view to helping forward the work.

"The Lethal Concentration of Acids and Bases in respect of *Paramæcium aurelia*."

By J. O. WAKELIN BARRATT, M.D., B.Sc., Lond., British Medical Association Research Student.

Communicated by Sir VICTOR HORSLEY, F.R.S. Received June 15,—Read June 16, 1904.

(From the Physiologisches Institut, Göttingen.)

The present investigation arose out of a research on chemiotaxis, in the course of which it became apparent that a pre-condition of the correct understanding of the nature of chemiotaxis is the quantitative determination of (1) the concentration of the acid and alkaline solutions employed for the study of chemiotactic phenomena, and also of (2) the absolute weight of Paramœcia (or other organisms) added to such solutions. So long as these data are unknown, chemiotaxis can only be investigated qualitatively, and such facts as are ascertainable solely by means of quantitative observations lie beyond the limits of research.

In order that the acid and alkaline liquids employed may be readily comparable one with another, equimolecular solutions are employed in this investigation. The absolute volume of Paramœcia employed in the different experiments was determined by means of the hæmocrit, as in the case of red blood-cells, and from this the weight of Paramœcia was ascertained. In those experiments in which an approximate determination of the weight was sufficient, the Paramœcia were counted, a modification of the method used for the enumeration of red blood-cells being adopted.

In all cases the Paramœcia were obtained in as nearly as possible the same condition. They were removed by centrifugalisation from the liquid in which they had been cultivated, and placed in a large bulk of distilled water for 24 hours before use. At the end of this time they were again concentrated, by centrifugalisation, into a small bulk of fresh distilled water, and were ready for use. In this way contamination of the acid and alkaline solutions employed was avoided, and the modification of chemiotactic reaction brought about by the medium used for cultivation was also, as far as possible, avoided.

The method of investigation adopted for determining the lethal concentration of acids and alkalies consisted in placing Paramœcia in solutions of gradually decreasing molecular concentration, arranged so as to form a geometrical series, each succeeding concentration being half that of the preceding, and noting the time at which death occurred. In all the experiments quoted, in order to make certain that the extremely dilute solutions employed were accurately prepared, their relative conductivity was determined. The latter was measured by the deflection of a sensitive galvanometer, when a fixed potential difference was established between platinised electrodes immersed in the acid and alkaline solutions employed.

The action of acids and bases upon Paramœcia is shown in Tables I and II. The acids employed are divided into three groups, according to the degree to which they are dissociated; the first consisting of the strong mineral acids, hydrochloric, nitric and sulphuric; the second including the organic acids, formic, lactic, oxalic, tartaric, citric and acetic, together with phosphoric acid; while the third group is made up of extremely weak electrolytes, namely, carbonic, carbolic, hydrocyanic and boric acids. Similarly the bases employed may be arranged in three groups: the first consisting of the strongly dissociated metallic alkalies; the second being represented by the feebly dissociated ammonium hydrate; and the third consisting of the extremely weak electrolyte anilin. In the second column of the tables, the figures in brackets represent the time, in minutes, which elapsed before all the Paramœcia employed were killed. The latter were added in the proportion of about thirty to every 10 c.c. of liquid, and did not appreciably affect the concentration. The temperature of experiment was 16° C. to 18° C.

In 0·0001 N concentration* the strong mineral acids are nearly equally lethal. Some of the weak acids of the second group, in the same concentration, are more lethal than the mineral acids, namely, acetic, lactic and oxalic acids; while others of the same group are less so, namely, phosphoric, citric and acetic. On the other hand the weak electrolytes are lethal in a considerably higher molecular concentration, reaching in the case of hydrocyanic acid 0·3 N.

Since the rate at which chemical change takes place is dependent upon ionic concentration, the dissociation co-efficient calculated from the conductivity (18° C.) or the dissociation constant (25° C.) is given, so far as the available data permit, in the third column of the tables, and the corresponding ionic concentration in the fourth column, the latter being the product of the concentration and dissociation coefficient.

The weak acids are more lethal in less ionic concentration than the strong acids, and the extremely weak electrolytes exhibit the smallest ionic concentration, that of phenol forming the limit of the series. Excluding phenol, however, it is seen that when the acids employed are arranged in the order of their dissociation (Table I), the diminution in ionic concentration proceeds at a much slower rate than the increase of molecular concentration.

The strong alkalies are similarly less toxic than the weak alkali, ammonium hydrate, and the latter again is considerably less so than

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* The concentration given in the tables is equivalent, except for carbonic and boric acids, which are regarded as binary compounds, and whose concentration represents gramme-molecules per litre.

Table I.

	Lethal concentration for *Paramæcium aurelia.*	Dissociation coefficient.	Corresponding H^+ ionic concentration.
Hydrochloric acid, HCl	0·0001 N. (50′)	> 0·98	0·000098 N.
Nitric acid, HNO_3	0·0001 (55′)	> 0·99	0·000099
Sulphuric acid, H_2SO_4	0·0001 (40′)	> 0·95	0·000099
Formic acid, HCOOH	0·0001 (11′)	0·75	0·000075
Lactic acid, $CH_3CHOH.COOH$	0·0001 (9′)	0·68	0·000068
Oxalic acid, COOH.COOH	0·0001 (9′)	—	—
Tartaric acid, COOH.CHOH.CHOH.COOH	0·0001 (35′)	—	—
Phosphoric acid, H_3PO_4	0·0001 (85′)	—	—
Citric acid, $\begin{matrix}\mathrm{COOH.CH_2}\\ \mathrm{COH.COOH}\\ \mathrm{COOH.CH_2}\end{matrix}$	0·0001 (60′)	—	—
Acetic acid, $CH_3.COOH$	0·0001 (85′)	0·30	0·000030
Carbonic acid, H_2CO_3	0·014 (35′)	0·0048	0·000067
Phenol, C_6H_5OH	0·01 (20′)	0·000114	0·00000114
Hydrocyanic acid, HCN	0·3 (15′)	0·000066	0·000020
Boric acid, H_3BO_3	0·225 (60′)	0·000061	0·000014

Table II.

	Lethal concentration for *Paramœcium aurelia.*	Dissociation coefficient.	Corresponding OH^- ionic concentration.
KOH..........	0·002 N. (60′)	0·96	0·00192 N.
NaOH..........	0·002 (40′)	0·98	0·00196
LiOH..........	0·002 (10′)	—	—
$Ca(OH)_2$........	0·002 (10′)	0·98	0·00196
$Sr(OH)_2$........	0·002 (5′)	0·98	0·00196
$Ba(OH)_2$........	0·002 (5′)	0·998	0·00199
NH_4OH........	0·001 (2′)	0·14	0·00014
$C_6H_5NH_2$.......	0·04 (15′)	0·000108	0·000004

anilin, whose ionic concentration ($4·3 \times 10^{-6}$N) is about one five-hundredth of that of lithium hydrate (1960×10^{-6}N) for a nearly equal lethal effect.

The metallic alkalies can be arranged in two periodic groups, the mean lethal concentration of the one (K, Na, Li) being greater than that of the other (Ca, Sr, Ba), when Paramœcia are killed in nearly equal times. Further, the lethal effect runs parallel to the periodic order of these metals, as is exhibited in Table III, in which the atomic weights are given, and the lethal periods repeated from Table II. When the hydrates of calcium, strontium and barium are employed in solutions of weaker concentration, so as to permit of a more accurate determination of the lethal period than is possible when observation extends over so short a period as 5 minutes, it can be shown that strontium hydrate is less toxic than barium hydrate, but the difference between the latter hydrates is much less than that between strontium and calcium hydrates. Similarly the difference in lethal character between sodium and potassium hydrates is much less marked than that between sodium and lithium hydrates. It is not possible, owing to

Table III.

Group I.	Death caused by 0·002 N. solution (Table II) in	Group II.	Death caused by 0·002 N. solution (Table II) in
Li, at. wt. 7	10 mins.	Ca, at. wt. 40	10 mins.
diff. 16		diff. 48	
Na, „ 23	40 „	Sr, „ 88	5 „
diff. 16		diff. 49	
K, „ 39	60 „	Ba, „ 147	5 „

their insolubility, to employ the remaining members of the above periodic groups in the present investigation.

The considerable difference in ionic concentration both of acids and of bases, for a nearly equal toxic effect, shows that such effect is not hydrolytic in character, for in such a case the concentration of H^+ or OH^- ions would be constant for each series. The relation between periodic grouping and lethal character, exhibited by strong alkalies, supports the view that the latter is dependent upon a chemical reaction not hydrolytic in character.

"Contributions to the Study of the Action of Sea-snake Venoms.—Part I."

By Sir Thomas R. Fraser, M.D., F.R.S., Professor of Materia Medica in the University of Edinburgh, and Major R. H. Elliot, I.M.S., on Special Duty for Snake Venom Research, under the orders of the Secretary of State for India. Received May 10,—Read June 9, 1904.

(From the Pharmacology Laboratory of the University of Edinburgh.)

(Abstract.)

The only important contributions to the literature of the subject with which we are acquainted, are those recently made to the Royal Society by Captain Leonard Rogers, I.M.S.

Whilst acknowledging the value of these papers, we desire to state that our work was planned before we saw them, and has in all respects been independent of them.

The venoms used in this research were those of two species of Sea-snakes :—

1. That of *Enhydrina Valakadien* (*a*) expressed in Madras by Dr. Pinto from the venom glands of freshly killed large snakes and sent to us in the dry state, and (*b*) extracted by us from the dried glands of small snakes which had been collected by the same gentleman, and,

2. That of *Enhydris Curtus*, prepared in the same way as the first-mentioned specimen, of which, however, only a small quantity was procured for us by Dr. Pinto.

The Minimum-Lethal Doses of the Various Specimens of Venom.

1. (*a*) Expressed *Enhydrina Valakadien* venom :—

M.L.D. for rats = 0·00009 gramme per kilo. of body weight.
for rabbits = 0·00006 " " " "
for cats = 0·0002 " " " "

The minuteness of these doses proves that sea-snake venom is the most lethal of all substances whose lethal power has been determined.

1. (*b*) *Enhydrina Valakadien* venom extracted by us from dried glands :—

This proved to possess a lethality rather less than half that of the expressed venom.

2. Expressed *Enhydris Curtus* venom :—

M.L.D. for rats—between 0·0005 and 0·0006 gramme per kilo.

The minimum-lethal doses for rabbits and cats likewise proved to be higher than those of the Enhydrina venom.

We mention this difference in lethality between Enhydrina and Enhydris venoms without laying stress on it, as we are unable to be certain that it was not due to some change which the Enhydris venom had undergone.

Comparison of the Relative Lethality of Enhydrina and Cobra Venoms for Various Animals.—An active specimen of Cobra venom was taken, the M.L.D.'s of which for rats, rabbits, and cats had been found to be 0·0005, 0·0006, and 0·010 gramme respectively, per kilo. of body weight of animal. Expressing the smallest M.L.D. in the case of each venom as the unit, we find the relative lethality for the different kinds of animals to be the following :—

Cobra venom, rats = 1 ; rabbits = 1·2 ; cats = 20.
Enhydrina venom, rabbits = 1 ; rats = 1·5 ; cats = 3·3.

The difference in the cat-rodent relationship is especially suggestive of a marked difference in the physiological actions of the two venoms, and the reversal of the rat-rabbit relationship is also of some significance, in the same connection.

Symptoms of Sea-snake Poisoning in Animals.—In the main these symptoms resemble those of cobraism, but the dyspnœa is more urgent, probably because the heart is not directly affected by the venom, as it is in cobraism.

We have observed that lid-rise of the lower lid is a constant sign in Enhydrina poisoning, as it is in the course of poisoning by the venom of the Cobra and Krait. It appears to be produced by an elastic rebound of the lid, caused by paralysis of its depressor muscle, probably central in origin, and it is closely comparable with the ptosis met with in cobraised men and monkeys.

Of the two points dealt with above, the first suggests a difference between the actions of Cobra and Enhydrina venoms, and the second a resemblance between their actions.

The Antagonism of Calmette's Serum and Enhydrina Venom Compared with that between Cobra Venom and the same Serum.—A sample of Calmette's serum which proved to be definitely antagonist to Cobra venom, exerted only a very feeble action against the venom of *Enhydris Curtus*. The venoms were mixed together and left in contact with the serum *in vitro* for half an hour before injection. We thus have obtained definite evidence of a chemical difference in the composition of the two venoms, from which differences in their actions may confidently be anticipated.

Methods of Experiment Employed.—These were:—

(1) Perfusion of the frog-ventricle with solutions of Enhydrina venom.

(2) Perfusion of the vessels of pithed frogs with solutions of Enhydrina venom.

(3) Kymographic experiments, in which the blood pressure, respiratory movements, etc., were recorded and studied, both before and after the intravenous injection of Enhydrina venom.

The movements of the auricle and ventricle were also studied during life by removing a portion of the chest wall, and attaching levers to the heart by hooks and silk threads. Venom was intravenously injected, and the results recorded and noted.

(4) The state of the phrenic, sciatic and vagal nerve-ends was studied immediately on the occurrence of death in animals which had received various lethal doses of Enhydrina and Enhydris venoms. The secondary current was used for this purpose, and the distance of the secondary from the primary coil, when a muscular contraction was observed, was noted and stated in millimetres.

(5) The medulla oblongata of rabbits was exposed and Enhydrina venom was dropped upon the medulla at the region of the respiratory centre. Respiratory movements were recorded on a drum, with the aid of a double stethograph.

Summary of Results.

(1) Enhydrina venom has no direct action on the walls of the arterioles, or at least has no action in any strength of solution which could be present in the blood of a human victim of Sea-snake bite.

(2) Enhydrina venom acts directly on the isolated frog ventricle, producing a tonic and stimulating effect, but this action is produced only by very strong solutions (1 : 5000). The heart-beat is quickened, and the result is therefore similar to that produced by very weak solutions of Cobra venom (1 : 1,000,000 or weaker).

(3) By experimenting with the mammalian heart exposed *in situ*, we have clearly shown that Enhydrina venom has no direct action on the vagal cardio-inhibitory centre. This affords a striking contrast to the condition observed in Cobra poisoning. In the latter case, the powerful tonic and stimulant action of the venom on the heart-muscle

(or more probably on its nerve-ends) is masked by equally powerful and direct stimulation of the cardio-inhibitory centre. In Enhydrina poisoning, on the other hand, the complete absence of cardio-inhibition leaves the feeble tonic action on the heart free to manifest itself, as appears to be displayed in several of our tracings. We cannot otherwise explain the increase in rate of the heart-beats which we have not infrequently met with in our experiments.

(4) Enhydrina venom has apparently no direct action on the vasomotor centre. Rogers found that on the injection of a Viperine venom, or of the venom of the Banded Krait (*Bungarus fasciatus*), into an animal, a marked fall of blood pressure occurred, which was of central origin. In an investigation made by one of us with Drs. Sillar and Carmichael (of the Materia Medica Laboratory, Edinburgh), it was found that a similar and powerful action is exerted by the venom of the common Krait (*B. cæruleus*). The absence of any such action by the venom of Enhydrina is therefore worthy of note.

(5) The blood-pressure curve in Enhydrina poisoning is a remarkably steady one, provided that moderate doses of venom are given and that care is taken to avoid the injection of large volumes of fluid into the blood vessels. This is due to the fact that the blood pressure is exposed neither to the influence of the rival forces which act on the heart so strongly in cobraism, nor to the direct vasomotor changes with which we have dealt in the preceding paragraph.

(6) The respiratory mechanism is that which is chiefly affected by Enhydrina venom. If large lethal doses are employed, such as Rogers appears to have confined himself to, respiration falls rapidly, and a considerable rise of blood pressure, asphyxial in origin, may precede death. The heart-beat then quickly slows, and blood pressure falls with corresponding rapidity.

Obviously, these are simply the phenomena of rapid asphyxiation. If, however, smaller doses of venom are employed, no marked rise in blood pressure occurs. The ordinary level is maintained until near the occurrence of death; the beat then slows, and the blood pressure falls. Here we have an expression of gradual cardiac failure, brought about by slowly progressive asphyxiation. The absence in slow Enhydrina poisoning of the large asphyxial rises of pressure, which are so characteristic of the final stages of Cobra poisoning, is readily explained by the fact that Enhydrina venom has no direct constrictive action on the walls of the arterioles, such as Cobra venom possesses.

(7) As to the part of the respiratory mechanism that is affected by Sea-snake venom, the rapidity with which respiration is affected, both when venom is injected into a vein, and also when it is applied directly to the medulla oblongata, leaves no room to doubt that the respiratory centre is directly acted on by the venom. On the other hand, we have shown that some degree of motor nerve-end paresis is constantly

present in animals dying from the effects of subcutaneous injections of this venom. We have also emphasised the fact that, in experiments carried out by dropping venom on the exposed medulla oblongata, we have failed to kill animals through the respiratory centre with their motor nerve-ends still undamaged. In this respect, we have shown that Enhydrina venom differs in its action from Cobra venom. It would therefore appear that, in poisoning with Enhydrina venom, motor nerve-end paresis plays a much greater part than it does in cobraism. It is not difficult to suppose that a blunting of the motor nerve-end mechanism, even though far from absolute, may seriously add to the embarrassment of a centre which has already been directly and gravely enfeebled. We hope to return to this and other points in a future communication.

In conclusion, we desire to express our sense of indebtedness to the India Office, to the Government of India, and last, but by no means least, to the Madras Government, for the assistance and facilities which they have given us in the carrying out of this research.

"On the Action of the Venom of *Bungarus cæruleus* (the Common Krait)."

By Major R. H. ELLIOT,[*] I.M.S., W. C. SILLAR, M.B., B.Sc., Lecturer on Experimental Pharmacology, Senior Assistant in the Materia Medica Department, University of Edinburgh, and GEORGE S. CARMICHAEL, M.B., Ch.B., Assistant in the Materia Medica Department, University of Edinburgh. Communicated by Sir THOMAS R. FRASER, M.D., F.R.S.

Received May 12,—Read June 9, 1904.

(From the Pharmacology Laboratory of the University of Edinburgh.)

(Abstract.)

The only previously recorded work known to us on this subject was performed by Captain L. Rogers, I.M.S., and his results were published at the beginning of the present year.

Experiments were performed by us in the Pharmacological Laboratory of the University of Edinburgh with the following results:—

I. We determined the minimum-lethal dose of the dried venom for frogs and small mammals, rats and rabbits only being chosen, as our stock of the venom was very limited. We found that the M.L.D. for the frog was about 0·0005 of a gramme per kilo., for the rat 0·001 gramme per kilo., and for the rabbit the remarkably low dose of 0·00008 gramme per kilo.

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[*] On special duty for Snake-venom research, under the orders of the Secretary of State for India.

II. We found that Calmette's anti-venomous serum in quantities sufficient to protect rats against ten minimum-lethal doses of Cobra venom, in the same quantities was quite powerless to protect these animals from similar doses of Krait venom.

III. We studied the condition of various nerve terminals, both in animals that die after poisoning by Krait venom and in nerve muscle preparations from the frog, and found that the integrity of these nerve ends was invariably involved at a comparatively early stage in the poison.

IV. The blood was carefully examined and no evidence of ante-mortem clotting or intravascular hæmolysis was discovered.

V. We examined the action of Krait venom when its solution was perfused through the isolated vessels and heart, respectively, of the frog. We found that this venom, while resembling in action that of Cobra venom, differs greatly in the degree of constriction of vessels and enhancement of ventricular contraction produced. Cobra venom exercises an action in these directions many times greater than that of Krait venom. Cardio-plethysmographic tracings are shown.

VI. Studying the manner in which the vital functions of mammals (rabbits, cats, and dogs) were influenced when exposed to the action of this venom, we show by means of kymographic and plethysmographic tracings that the vaso-motor centre is strongly affected, a suspension of the activity of this centre, as shown by the great splanchnic dilatation, rapidly ensuing after its transient stimulation. There are also indications of a feeble cardio-inhibitory action. The experiments and illustrative tracings likewise show that death is brought about by destroying the activity of the respiratory centre.

VII. From these results the conclusion may be arrived at that while the symptoms produced by Krait poisoning are similar to those of Cobra poisoning, they differ so much in relative degree as to render it doubtful if they can properly be spoken of as identical.

"The Decomposition of Ammonia by Heat." By E. P. PERMAN, D.Sc., and G. A. S. ATKINSON, B.Sc. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S. Received May 3,—Read June 16, 1904.

This subject has been already dealt with by Ramsay and Young,* who heated ammonia in glass tubes at various temperatures, and found that decomposition began under the most favourable circumstances at a little below 500°, and that the amount decomposed depends on the extent of the heated surface of the solid with which the ammonia is in contact, on the nature of the surface, and on the time of exposure to heat.

We have thought it desirable to extend our knowledge of the subject still further by investigating the *rate of decomposition* at various temperatures. The ammonia was contained in porcelain vessels heated in a muffle furnace, and the decomposition was traced by reading the pressure on a mercury manometer, the sum of the volumes of the ammonia and products of decomposition being kept constant. The difficulty of finding the amount of ammonia in the vessel at the beginning of the decomposition was overcome by heating the ammonia at the *end* of a series of observations until complete decomposition was caused; the pressure and temperature were then noted, and the original amount of ammonia calculated. We have confirmed the observations of Ramsay and Young that the decomposition is never absolutely complete, but after heating at a temperature of 1100° for a short time the amount of ammonia remaining is so small that it can be neglected for practical purposes.

Apparatus.—The ammonia was heated in a porcelain globe A (fig. 1) of about 2 litres capacity by means of a muffle furnace B; the capillary stem of the globe was connected with a capillary glass tube by a copper sleeve and some fusible alloy. The pressure gauge D stood 2 metres high, and the level of the mercury was regulated by a movable reservoir F. The pressure was read on a millimetre scale; G is a movable piece of mirror glass of rectangular shape, and with a horizontal line drawn across it; by sliding it along the edge of the millimetre scale and behind the glass tubes of the gauge, the readings were made with great facility.

H is a U-tube with a stop-cock at the bottom; its object was to cut off the ammonia from the three-way stop-cock *k* by a column of mercury, and so prevent or indicate leakage. One branch of the stop-cock *k* led to a water-air pump, and the other to a long tube L containing caustic soda, and thence to a cylinder of ammonia with a safety escape M, consisting of a tube dipping into a column of mercury.

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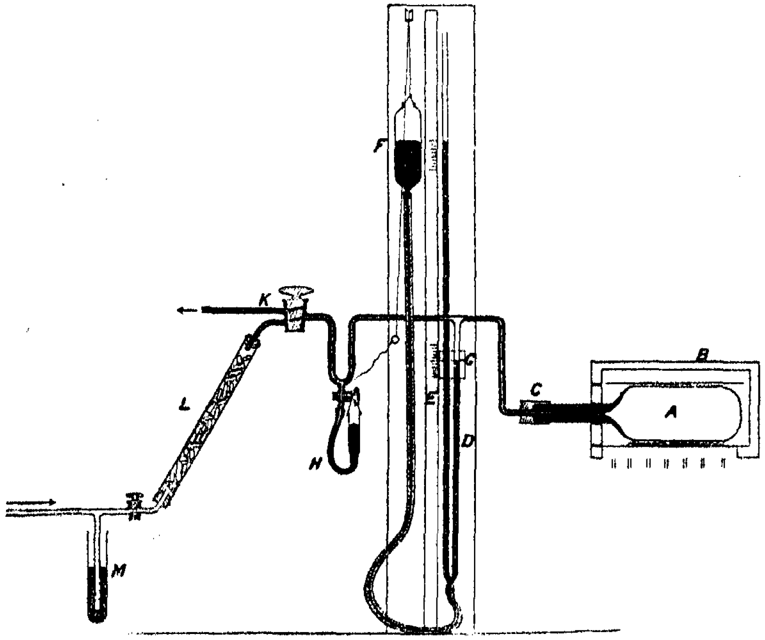
* 'Chem. Soc. Journ.,' vol. 44, p. 88, 1884.

Measurement of Temperature.—Temperature was measured by means of a Callendar-Griffiths pyrometer. The disturbing effect of the current of hot air passing over the projecting head of the thermometer was avoided by surrounding the head with several turns of tinned iron. The temperatures were read to 0·1° C. The thermometer was carefully standardised with melting ice, boiling water, and boiling sulphur, and we do not think that the temperature error can in any case exceed 0·5° C.

Fig. 1.



Thermostat.—To maintain the temperature constant an Ostwald pattern regulator was used, the vessel being of porcelain and containing air. In addition to this a Fletcher gas regulator was fixed on the main supply. Any variation of temperature caused by alteration of the barometric pressure was corrected by means of a screw at the bottom of the U-tube containing the mercury. It was found convenient to adjust the gas supply to give the required temperature by loading the valve of the Fletcher regulator.

Material.—The cylinder of ammonia was obtained from the Standard Anhydrous Ammonia Company, and was found to contain but very little impurity. In one experiment about 20 litres of ammonia were passed slowly through a long worm surrounded by ice and hydrochloric acid, but nothing appreciable was condensed. The gas was found to be free from carbon dioxide. A quantity of pure hydrochloric acid was neutralised by passing the gas from the cylinder through it, and the solution was then evaporated to dryness. Chlorine was then estimated in the sample by the gravimetric method, and the percentage found was (1) 66·09; (2) 66·12; mean, 66·105; theoretical, 66·23.

Method of Work.—The furnace was heated, and when the temperature was sufficiently constant, the filling process was commenced. The globe was exhausted, and ammonia admitted from the cylinder through the drying tube L; this was repeated from eight to ten times, when the filling was regarded as complete. Readings of pressure were then made at definite time intervals, and the temperature was also carefully noted, as nearly as possible at the same time, by means of the pyrometer. In one or two of the experiments the temperature was sufficiently high to decompose the ammonia completely in a short time, but in most of them, when a sufficient number of readings had been made, the temperature was raised until (practically) complete decomposition ensued in a few minutes. The volume of the ammonia and decomposition products was kept constant by raising the mercury reservoir F so as to keep the mercury at about the same level in the upper part of the short limb of the pressure gauge. As each time interval was called, the level of the mercury in D was read, and that in the open limb as soon as possible afterwards; it did not change quickly in the latter, owing to the width of the reservoir.

Some observations were also made on the effect produced by sudden change of pressure on the rate of decomposition.

Method of Calculation.—The ultimate decomposition of ammonia is customarily represented by the equation $2NH_3 = N_2 + 3H_2$. Let p_1 be the pressure of the ammonia in the globe at any instant during the decomposition, p_1', that of the nitrogen, p_2', that of the hydrogen, P, the total pressure at the same *instant*, p_0, the initial pressure of the ammonia at the beginning of the experiment.

Then $$p_1 + p_1' + p_2' = P \quad \text{......} \quad (1),$$

also $$p_2' = 3p_1' \quad \text{......} \quad (2),$$

and $$p_1' + p_2' = 2(p_0 - p_1) \quad \text{......} \quad (3);$$

expressing that (1) the sum of the partial pressures is equal to the total pressure; (2) the pressure of the hydrogen produced is three times that of the nitrogen; (3) the sum of the pressures of the nitrogen and hydrogen is double the pressure of the ammonia decomposed.

From this it follows by substitution that $p_1 = 2p_0 - P$, *i.e.*, the pressure of the ammonia at any instant is double the initial pressure minus the total pressure at the instant of observation. The experimental data furnish values of P and $2p_0$, and $2p_0 - P$ has been tabulated giving the pressure of ammonia at the time of observation. From these numbers corresponding values of $\Delta P/\Delta t$ have been calculated by taking the mean of the two consecutive differences and dividing by the time interval; but $\Delta P/\Delta t = dP/dt$ approximately within the limits of experimental error, and $dP/dt = dp_1/dt$, and therefore we have the rate of change of the pressure of the ammonia at definite pressures, they have been plotted in two series of curves.

Results.—The rate of decomposition was found to be much influenced by the state of the globe; it invariably increased after the globe had been used once or twice, owing probably to the action of ammonia or hydrogen upon the porcelain; consequently we were not able to trace the effect of temperature on the rate of decomposition. In the first experiments the projecting stem of the globe was allowed to become too hot, with the result that a trace of the alloy at the joint C found its way into the globe, and by its catalytic action increased enormously the rate of decomposition of the ammonia. The alloy contained a small proportion of mercury, and a film of this metal was found on the interior of the globe when it accidentally broke. In the later experiments great precautions were taken to maintain the stem of the globe at a low temperature. The experiments are here tabulated to serve as a key to the curves.

Mean temperature.	Greatest variation of temperature.	Remarks.
791°	± 0·2°	Traces of mercury present.
750	0·6	,, ,,
841	0·2	New clean globe, pressure fell only 20 mm. in 2 hours.
894	0·6	Globe as from last experiment.
833	1·1	,, ,,
1111	0·35	Globe freshly cleaned.
902	0·8	,, ,,
1061	0·6	Globe as from last experiment.
815	0·4	,, ,,
797	1·0	Iron wire in globe.
1025	0·4	Pt. black in globe.

The measurements made at 1111° and 1025° are given in full; they may serve as samples.

Mean Temperature 1111°.

Time. mins.	Total pressure (P). mm.	$2p_0 - P$.	dp_1/dt.
0	1047·4	330·1	—
2	1140·7	236·8	39·2
4	1204·3	173·2	27·4
6	1250·4	127·1	20·6
8	1286·8	90·7	15·5
10	1312·3	65·2	11·4
12	1332·5	45·0	8·35
14	1345·7	31·8	6·0
16	1356·4	21·1	4·2
18	1362·6	14·9	2·7
20	1367·1	10·4	2·35
22	1372·0	5·5	—
32	1377·5	0·0	—
42	1377·5	0·0	—

It will be noted that in this experiment the decomposition was completed without raising the temperature.

Globe rinsed with a solution of platinum chloride and heated to bright redness. Mean Temperature 1025°.

Time. mins.	Total pressure (P). mm.	$2p_0 - P$.	dp_1/dt.
0	1126·1	242·4	—
2	1195·8	172·7	27·95
4	1237·9	130·6	17·4
6	1265·4	103·1	12·0
8	1285·9	82·6	9·05
10	1301·6	66·9	7·2
12	1314·8	53·7	5·8
14	1324·9	43·6	4·6
16	1333·2	35·3	3·7
18	1339·7	28·8	3·1
20	1345·5	23·0	2·5
22	1350·8	17·7	2·1
24	1354·8	13·7	2·0
26	1358·9	9·6	1·9
28	1362·5	6·0	—

$2p_0$ is taken as 1368·5, which was obtained by extrapolation of the time-pressure curve.

These results are best understood from the curves shown in fig. 2 and fig. 3, having values of dp_1/dt as ordinates and of p_1 as abscissæ.

Fig. 2 shows the lower and fig. 3 the higher ratio of decomposition. The curves, as a rule, do not depart much from straight lines, and at the highest temperatures, 1061° and 1111°, become straight lines or

FIG. 2.

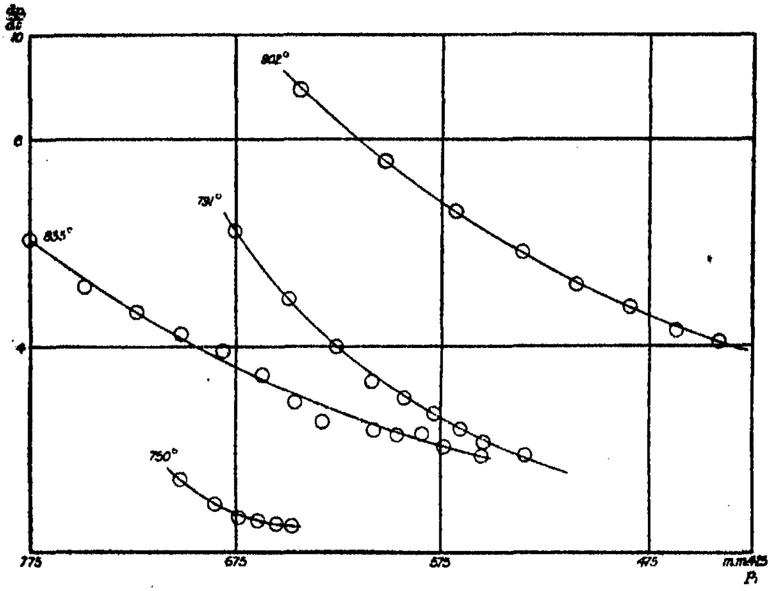
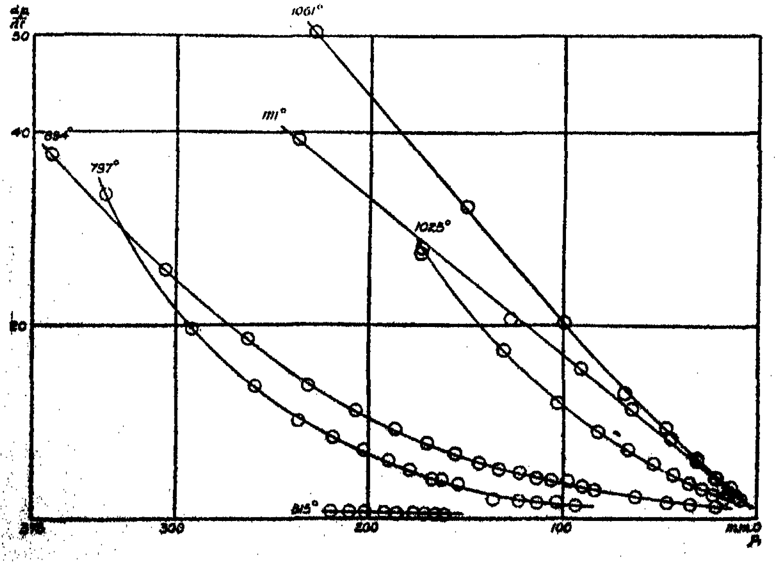


FIG. 3.



very nearly so. These results indicate that at the highest temperatures the decomposition is of the first order, *i.e.*, it is monomolecular, proceeding according to the equation $NH_3 = N + 3H$; the union of the atoms to form molecules is probably so quick that it can be neglected when compared with the rate of decomposition of the ammonia molecule. The departure from this mode of decomposition at lower temperatures is possibly caused by the volume and mutual attraction of the molecules. No formula has yet been devised to express the results satisfactorily.

In the presence of substances having a catalytic action, the resulting curve is altered in character, the curvature being greater at the higher pressures. This is well shown in the curves at 750° and 791° (fig. 2), mercury vapour being present, and in those at 797° and 1025° (fig. 3), when iron wire and platinum black respectively were present. In these two latter experiments it will be noticed that the rates of decomposition reached and passed those without catalyser for about 100° higher.

Effect of Sudden Change of Pressure on the Rate of Decomposition.

As a final experiment the effect of a sudden change of pressure was tried, the globe containing both iron wire and finely divided platinum. The change of pressure was brought about by allowing the gases in the globe to blow off into the air for a few seconds, and a reading of the pressure gauge was made as soon as possible afterwards.

Time.	Pressure gauge.	Bar.	Total pressure.	ΔP.
7·4	335·2	760·8	1096·0	20·8
9	356·0	,,	1116·8	19·6
14	375·6	,,	1136·4	
7·16	58·2	760·9	819·1	15·2
21	73·4	,,	834·3	14·7
26	88·0	761·0	849·0	

The ratio of the pressures before and after the change is 1136·4/819·1 = 1·39, and that of the ratio of decomposition (taken approximately from the values of ΔP) is 19·6/15·2 = 1·29.

The agreement is sufficiently close to show that the reaction is essentially of the first order, or monomolecular, apart from the little-understood disturbing influences.*

Summary and Conclusion.

The rate of decomposition of ammonia has been investigated under various conditions; the containing vessel was of porcelain. The temperatures varied from 677° to 1111°. It was found that the reaction is essentially monomolecular, being similar to that for arseniuretted hydrogen, as found by van't Hoff. The rate of decomposition is much quickened by the presence of traces of some of the metals, those tried being mercury, iron, and platinum.

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* See van't Hoff's 'Vorlesungen,' 2nd edition, p. 234.

We are indebted to the Government Grant Fund of the Royal Society for the cost of most of the apparatus employed, and wish to express our great obligations to Principal Griffiths for the loan of some of his apparatus for platinum thermometry, and for his kind guidance in its use.

Supplementary Note, May 27, 1904.—We have assumed that the decomposition of ammonia is an irreversible reaction, *i.e.*, $k' = 0$ in the general formula $dx/dt = k\,(a-x)\,(b-x)\,\ldots\,-k'\,(a'+x)\,(b'+x)\,\ldots$ for Ramsay and Young showed* that on passing a mixture of dry nitrogen and hydrogen through a heated glass tube containing iron filings, or through a red-hot iron tube, no appreciable quantity of ammonia was formed, a result which we confirmed by experiments of our own some years back, obtaining the same result also with a glass tube containing porcelain. We find, however, that this view of the matter is not generally accepted; Ostwald, for instance, in his 'Grundlinien der anorganischen Chemie'† states that, on heating ammonia, equilibrium ensues when 98 per cent. of the ammonia is decomposed. We should like to point out that the results of our experiments, now described, show no indication whatever of any such equilibrium, for the curves all run towards the origin within the limits of experimental error, whereas, if there were any equilibrium before the ammonia was all decomposed, they would cut the horizontal axis to the left of the origin, and, moreover, the equilibrium would change with the temperature.

We have mentioned that a trace of ammonia was always found in the globe at the end of an experiment, but this probably came from the cold stem; and, moreover, since the rate of decomposition may be taken as proportional to the amount of ammonia present, that amount can, strictly speaking, never quite reach the zero point.

Whether a minute quantity of ammonia remains finally undecomposed would not be indicated by these results, and we intend to approach the subject from another direction, and to examine generally the conditions under which nitrogen and hydrogen combine to form ammonia.

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[*] *Loc. cit.*

[†] 1900, p. 345.

"An Experiment Illustrating Harmonic Undertones." By HERBERT KNAPMAN, B.A., Fellow of Emmanuel College, Cambridge, and Assistant Lecturer in Mathematics at University College, Reading. Communicated by GEORGE J. BURCH, D.Sc., F.R.S. Received June 6,—Read June 16, 1904.

An Experiment Illustrating Harmonic Undertones.

The object of this note is to describe a phenomenon of which, as far as I have been able to learn, no published account has hitherto been given, although perhaps its extreme simplicity renders it unlikely that it has altogether escaped detection. If a vibrating tuning-fork is pressed against a light object, such as a piece of paper or a stretched string, this object will in general follow the vibrations of the fork until they die away, remaining in contact with the fork all the time. This method of using a tuning-fork is mentioned in Lord Rayleigh's "Theory of Sound," § 133. If, however, a piece of paper is touched lightly by the vibrating fork, the elastic force opposing displacement of the paper may be so small that it does not remain in contact with the fork, but is driven away by the tap which it receives. The paper may return in time to be struck by the fork before the latter has executed a complete vibration, and the process being repeated again and again the paper will vibrate with the same period as the fork, but with a motion which is not simple-harmonic, on account of the irregularity caused by the blows. The result of this is that the paper emits a note in which the harmonic overtones are of considerable importance, and which, therefore, resembles the note of a bowed violin string rather than the almost pure tone of the tuning-fork. This resemblance is easily perceived, as is also the change to the approximately pure tone which takes place when contact ceases to be broken, on account of increase of pressure or falling off in the amplitude of vibration of the fork. (The vibration of the air in the neighbourhood of the fork has also an effect on the motion of the paper, but this effect is probably so small in comparison with that of the blows that it may here be omitted.)

If the paper does not come within striking range of the fork again until the latter has nearly had time to execute two complete vibrations, the note given by the paper will be an octave below that of the fork, since the vibrations of the paper have now a period which is double that of the fork. Thus, supposing the pitch of the fork to be *c''*, the paper will give the note *c'*. If the fork strikes the paper at every third vibration the paper will give *f*, a twelfth below the note of the fork. Similarly contact at every four, five, six, or seven vibrations will give *c*, A♭, F, or a note a little sharper than D, the ratio of their frequencies being 64 : 63. We can thus obtain from the paper the series of harmonic undertones

c′, *f*, *c*, A♭, F, D +, C, B,♭, A,,♭, etc.

It is easy to obtain about the first ten of these when a small slip of paper is used and is held close to the ear. There is some difficulty in making the lower notes audible on a large scale without depriving the experiment of the simplicity which is probably its chief merit; it is perhaps best to use a large sheet of paper suspended in a vertical plane with one edge pasted to a vertical edge of an empty wooden box which may reinforce the sound. The tuning-fork can be held in the hand or clamped so as to touch the paper near its edge; the undertone usually given will vary with the position of the point of contact. The effect might be prolonged for any time by using an electrically maintained fork.

Some further information as to the behaviour of a light object under the influence of a series of periodic blows was obtained by means of a large steel tuning-fork with prongs about a foot long, which was clamped in such a position that one of its ends, vibrating horizontally, struck the upper end of a small vertical card (usually an ordinary visiting card), the lower end of which was fixed, so that the card behaved somewhat as a clamped-free rod of considerable width in comparison with its length. The average pressure and the position of the point of contact could be varied at will. The fundamental pitch of the fork was itself so low that harmonic undertones, produced by the card in the way described above, were practically inaudible; the nature of the vibration was, however, examined by looking through a lens at the upper edge of the card against a dark background. The edge appeared to be drawn out into a continuously shaded band, in which occurred at intervals somewhat abrupt white lines, indicating positions at which the card was nearly or quite stationary. When contact was being broken several of these lines were usually visible, and it was possible to get them to remain steady, though sometimes they flickered rapidly. The line at the end of the band nearest the fork was usually very faint, often practically invisible, which points to the suddenness with which the card is driven away from the fork when they come into contact.

The presence of these white lines shows that the card executes vibrations corresponding to more than one of its free modes, and that the resultant vibration differs considerably from the simple harmonic form. (This agrees with the audible presence of harmonics in the experiment first described, where a sheet of paper is struck by an ordinary tuning-fork.)

As the vibrations of the large fork diminish in amplitude the white lines become fewer, until generally only two or one remain in the interior of the band, in addition to the line at the end of the band away from the fork. If the amplitude of the fork dies down still further or the pressure between the card and the fork is increased, the lines disappear from the interior of the band and that at the end next to the fork becomes as strongly marked as the line at the other end. This, of course, indicates that contact has ceased to be broken, and the only audible note given by the card is now the fundamental note of the fork.

"Further Note on the Remains of *Elephas cypriotes*, Bate, from a Cave-Deposit in Cyprus." By Dorothy M. A. Bate. Communicated by Dr. Henry Woodward, F.R.S.

Received April 18,—Read June 9, 1904.

(Abstract.)

This paper is a continuation of one *already published*,* "On the Discovery of a Pigmy Elephant in the Pleistocene of Cyprus," and enters into a detailed description of the teeth of this small proboscidean, whose remains are now in the British Museum of Natural History.

The collection includes incisors, milk molars, and permanent molars. Several of the latter still retain their position in the jaws and, in some instances, the teeth of both sides of the same individual were found.

The permanent incisor tusks of two forms, presumably belonging to males and females, were found. They differ from the same teeth of the Maltese dwarf elephants in being considerably compressed laterally. The largest specimen measures 29·7 cm. along the outside of the curve, with a maximum diameter of 3·7 cm.

Of the upper cheek teeth the third and fourth of the milk series as well as the three permanent molars are described in detail. There was a small third milk molar (mm. 2) implanted by a single root, but no specimen was collected. Of the lower series the third and fourth milk molars and the three permanent teeth were represented by numerous examples and are fully described. An almost entire left ramus of one young individual and the symphysial portion of another are also described. The only limb bone obtained was the distal portion of a femur.

A corrected ridge formula for the molars of *E. cypriotes* is furnished, which, exclusive of talons, will stand as follows:—

$$\div,\ \frac{5}{5},\ \frac{7-8}{7-8},\ \frac{7-8}{7-8},\ \frac{8-9}{8-9},\ \frac{11-12}{11-12}.$$

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* Read before the Royal Society, May 7, 1903.

Dr. Leith Adams gives *E. melitensis* as follows:—

$$\frac{3}{3}, \frac{5}{5}, \frac{8\text{—}9}{8\text{—}9}, \frac{8\text{—}9}{8\text{—}9}, \frac{10}{10}, \frac{12}{12}.$$

There appears to be a strong resemblance between the teeth of *E. cypriotes* and those of the Maltese and Sicilian pigmy forms, more especially *E. melitensis*, but the marked lateral compression of the tusks in *E. cypriotes*, which is a constant character in all the specimens so far obtained, would in itself be almost sufficient to distinguish this species from the other pigmy elephants of the Mediterranean region. There seems to be good evidence that *E. cypriotes* was isolated and subsequently differentiated at an earlier period than the other small Mediterranean species in Malta and Sicily, the zoological evidence giving considerable support to the belief that Cyprus became an island at an earlier period, an idea which is further strengthened by the fact that the whole island is surrounded by deep water, and is not connected with the neighbouring lands by submerged banks as is the case with the Maltese Islands.

The Maltese pigmy species have been considered most closely allied to *E. antiquus* and *E. Africanus*. On the other hand it seems probable that *E. cypriotes*, which shows no affinity to the African species, is rather connected with *E. antiquus* and *E. meridionalis*.

It may be remarked that the remains of *E. cypriotes* and of *Hippopotamus minutus*, with which it is associated, vary but little in size, whereas in the dwarf species of elephants and hippopotami from Malta and Sicily a considerable variation in size is observable, so much so indeed that molars may be seen intermediate in size connecting *H. melitensis* (= *minutus*), *H. pentlandi* and *H. amphibius*.

"The Absorption and Thermal Evolution of Gases occluded in Charcoal at Low Temperatures." By Sir JAMES DEWAR, M.A., D.Sc., LL.D., F.R.S., Jacksonian Professor, University of Cambridge, and Fullerian Professor, Royal Institution, London. Received June 15,—Read June 16, 1904.

During the year 1874—5, in association with the late Professor Tait, a research was undertaken which involved the production of very perfect vacua, and with the object of improving on the then known methods, dense charcoal was employed as an efficient absorbent of traces of any gaseous residuum.

An account of these experiments communicated to the Royal Society of Edinburgh appeared in 'Nature,' July 15, 1875, under the title of "Charcoal Vacua."

In Professor Clerk Maxwell's Notes on "Molecular Physics" the following succinct description of the process is given:—

"Another method employed by Professor Dewar is to place in a compartment of the vessel a piece of freshly heated cocoanut charcoal, and to heat it strongly during the last stages of the exhaustion by the mercury pump. The vessel is then sealed up, and as the charcoal cools it absorbs a very large proportion of the gases remaining in the vessel.

"The interior of the vessel, after exhaustion, is found to be possessed of very remarkable properties.

"One of these properties furnishes a convenient test of the completeness of the exhaustion. The vessel is provided with two metallic electrodes, the ends of which within the vessel are within a quarter of an inch of each other. When the vessel contains air at the ordinary pressure a considerable electromotive force is required to produce an electric discharge across this interval. As the exhaustion proceeds, the resistance to the discharge diminishes till the pressure is reduced to that of about a millimetre of mercury. When, however, the exhaustion is made very perfect the discharge cannot be made to take place between the electrodes within the vessel, and the spark actually passes through several inches of air outside the vessel before it will leap the small interval in the empty vessel. A vacuum, therefore, is a stronger insulator of electricity than any other medium."

At one of the conferences held in connection with the Special Loan Collection of Scientific Apparatus* in the year 1876, I showed that with a vapour like bromine the absorptive power of the charcoal was so effective that a space filled with the vapour even at atmospheric pressure could be made into a fairly high vacuum showing very wide striæ.

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* See 'Science Conferences,' "Physics and Mechanics," p. 154.

When the charcoal was heated the bromine vapour was again expelled, and on allowing it to cool, all stages in the appearance of the electric discharge as the vacuum is reached could be conveniently observed without the use of any form of air-pump.

When in the course of low temperature investigations the perfection of the vacuum vessels for the storage and manipulation of liquid air and hydrogen came to be important, the effect of charcoal on heat isolation in such utensils was fully investigated and confirmed in a paper entitled "Liquid Air as an Analytic Agent."* Still no systematic experiments on the absorptive power of charcoal at low temperatures were made either at this time or subsequently.

It is the object of the present preliminary paper to contribute some definite quantitative data regarding gas absorption and thermal evolution in charcoal at the temperature of liquid air. The mode in which liquid gases like oxygen or air could be used as calorimetric agents was described in my paper on the "Scientific Uses of Liquid Air."†

The apparatus was further improved into the form illustrated and described in Madame Curie's Work, "Recherches sur les Substances Radio Actives," 2nd edition, p. 100, as used for the determination of the heat evolved by radium bromide either in liquid oxygen or hydrogen. Such calorimeters are easily adapted to the simultaneous observation of the volume of any gas absorbed by charcoal, and of the concomitant heat evolution.

For this purpose a small glass bulb C containing from 0·5—1 gramme of charcoal has a long narrow tube C attached, so that it can be immersed in the liquid oxygen or air in the calorimeter A B, while still allowing a part of the tube to project above the cork A. In order to dry and cool the 40 c.c. of gas, which represents the largest volume taken in by the charcoal in my experiments, a little annular space is arranged at D into which liquid air is poured immediately before the experiment is made.

The charcoal, after being placed in the tube C, is heated to a low red heat and simultaneously exhausted by a good air-pump, and after all the gas has been removed the stop-cock E is closed. In this condition it is placed in the calorimeter.

The experiment is conducted by connecting the end of the tube at E by means of an india-rubber tube with a graduated vessel F containing the gas. When all is ready the stop-cock E is opened, so that the gas may rush into the charcoal, and the heat evolved by its absorption distils off the equivalent quantity of liquid air from the calorimeter, which is measured in the vessel G.

The constant of the calorimeter being known (which with liquid air is about 14·5 c.c. per calorie), we get the actual thermal evolution together with the volume of gas absorbed.

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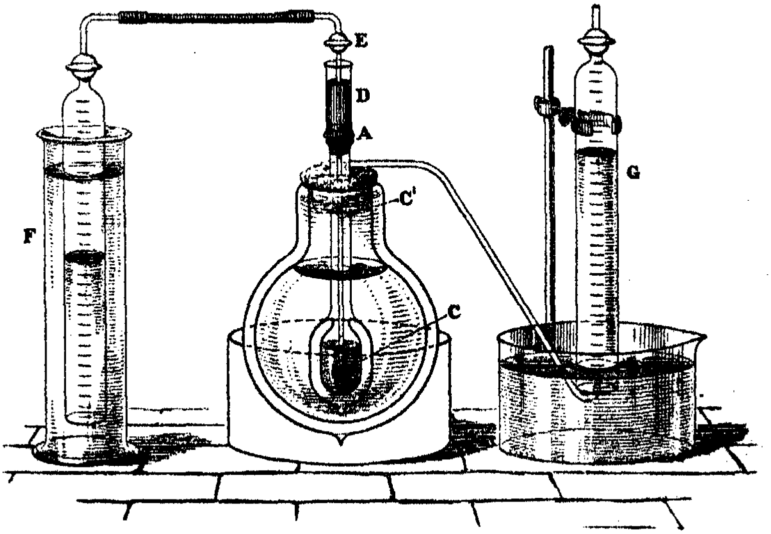
* 'Roy. Inst. Proc.,' 1898.

† 'Roy. Inst. Proc.,' 1894.

The heat correction for the rush of gas into the same exhausted glass bulb without charcoal is small in proportion to the total heat evolved, and the same may be said of the volume correction on account of the cooling of the space external to the charcoal. With a variable material like cocoanut charcoal I have in the calorimetric experiments used the same sample in all cases. The following table embodies the general results per cubic centimetre of charcoal. The gas absorption is given at 0° and 760 mm. If the volume of gas absorbed had been measured under the same conditions of pressure at −185° C., then the numbers in Column II would all have to be divided by three.



	I. Volume absorbed. 0° C.	II. Volume absorbed. −185° C.	III. Heat evolved. Gramme calories.
Hydrogen	4 c.c.	135 c.c.	9·3
Nitrogen...............	15 „	155 „	25·5
Oxygen	18 „	230 „	34·0
Argon..................	12 „	175 „	25·0
Helium	2 „	15 „	2·0
Electrolytic gas	12 „	150 „	17·0
Carbonic oxide and oxygen	30 „	195 „	34·5
Carbonic oxide	21 „	190 „	27·5

In all cases, it will be observed, the amount of gas occluded has been greatly increased at the low temperature, and the degree of condensation is generally such as we should anticipate from the known physical constants of the gases. The amount of heat evolved is so great as to be in excess of that required for liquefaction in the case of gases like hydrogen, nitrogen, and oxygen. The heat produced when successive fractions of the volume of gas required for saturation are absorbed has yet to be determined. In the time required for the absorption no measurable amount of chemical combination was effected between mixtures of hydrogen and oxygen or carbonic oxide and oxygen in the pores of the charcoal.

Such experiments must be extended to the use of platinised charcoal and other catalytic agents.

Perhaps the most striking result is the great difference in properties exhibited by helium. While resembling the other gases in showing increased absorption at the temperature of liquid air, the absolute amount occluded per unit volume of charcoal is about one-tenth that of the other gases at the same temperature. There can be little doubt that when the relative absorption of helium in charcoal is measured at the temperature of liquid hydrogen, the increased absorption will be so marked as to make it comparable to that of hydrogen in the present set of experiments. In this case charcoal at the boiling point of hydrogen will become an efficient condensing agent for helium, and this property will have important applications in future research.

Separation of Highly Concentrated Oxygen from Air.

In order to examine the changes taking place in a mixed gas like air during the absorption, a quantity of about 50 grammes of charcoal was after heating and exhaustion saturated at − 185° in a current of pure dry air; got by passing the air current through a U-tube immersed in liquid air.

For a time the air rushed into the charcoal with great rapidity, and in about 10 minutes between 5 and 6 litres were taken in. A manometer attached to the vessel containing the charcoal showed, on shutting off the air current, that during the early part of the saturation the absorption was so effective as to give practically no measurable mercury pressure. As soon as the absorption was ended, and a current began to pass slowly over the charcoal, the composition of the air leaving the charcoal showed 98 per cent. nitrogen. After the current of air had passed for half an hour, the total gas occluded in the charcoal was expelled by taking the vessel in which it had been treated out of the liquid air, and allowing the temperature to rise to 15° C.

The gas, which was rapidly expelled, measured 5·7 litres, and contained 56 per cent. of oxygen. If the saturated charcoal before heating up was subjected for an hour to the action of an air-pump, capable of giving a steady exhaustion of 5 mm., no difference was effected in the oxygen percentage of the evolved gas. The same experiment was repeated with this variation, that, instead of the air current having the pressure of the atmosphere, it was kept below one-tenth of an atmosphere. In this experiment, 4·8 litres were expelled on heating up, and the percentage of oxygen was 58. Then, a further repetition was made with an air current supplied at a pressure not exceeding 5 mm. of mercury. After 3 hours' treatment, the charcoal, on heating to 15° C., gave 4½ litres of 57 per cent. oxygen. From these experiments it follows that the tension of the occluded gases, at the temperature of liquid air, must be very small, and thus the use of low temperatures, combined with charcoal, introduces a new and greatly improved means of getting high vacua, which in the future may be found susceptible of important practical applications. These experiments are quite conclusive as to the practical constancy of the mean composition of the air gases occluded in the charcoal (subject to the conditions aforesaid), and they further show that wide changes in the pressure of the air current has little or no effect in altering the proportions. In another experiment, the vessel containing the saturated charcoal, instead of being allowed to rise rapidly in temperature, was transferred to a vacuum vessel, in which a little liquid air was placed, in order that the temperature might rise slowly, and thereby enable the successive litres of gas given off to be collected separately and analysed.

This experiment gave the following results :—

		Oxygen per cent.
First litre	....	18·5
Second ,,	....	30·6
Third ,,	....	53·0
Fourth ,,	....	72·0
Fifth ,,	....	79·0
Sixth ,,	....	84·0

The mean composition of the 6 litres is again 56 per cent. oxygen. From the above experiments it follows that one of the most rapid means of extracting a high percentage of oxygen from atmospheric air is to absorb it in charcoal at low temperatures, and then to expel it either rapidly or slowly by heating the mass of charcoal to the ordinary temperature.

A few experiments have been made using, instead of air, special mixtures of oxygen and nitrogen. Thus it was found that a gas containing 6·5 per cent. of oxygen used in the same manner as in the air occlusion experiments, gave, on heating up the charcoal rapidly to 15° C., 5 litres of gas having the composition of 23 per cent. of oxygen.

A repetition of the same process with the 23 per cent. of oxygen would have raised the percentage about 60 per cent., or a stronger concentration could have been reached by fractionating the gas as it slowly leaves the charcoal on gradually increasing the temperature.

This preliminary investigation suggests many fields for further inquiry, and some of these I hope to deal with in future papers.

I have to express my thanks to Mr. Robert Lennox, F.C.S., for efficient aid in the conduct of the experiments, and Mr. J. W. Heath, F.C.S., has also rendered valuable assistance.

"The Separation of the most Volatile Gases from Air without Liquefaction."

By Sir JAMES DEWAR, M.A., D.Sc., LL.D., F.R.S., Jacksonian Professor, University of Cambridge, and Fullerian Professor, Royal Institution, London.

Received June 15,—Read June 16, 1904.

From the time when liquid air came to be an ordinary laboratory agent, I have continually used it for the purpose of producing high vacua in vessels that had been previously filled with easily condensable gases, like sulphurous acid, carbonic acid, vapour of water or benzol.

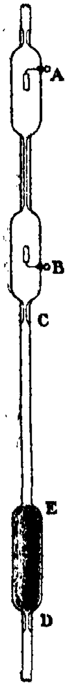
When the liquefaction of hydrogen was effected one of the first scientific uses to which it was put was that described in my paper on the "Application of Liquid Hydrogen to the Production of High Vacua, together with their Spectroscopic Examination."* In that communication it was shown by theory and confirmed by experiment that the condensing power of liquid hydrogen is so great relatively to that of liquid oxygen or nitrogen, that any closed vessel, a part of which is cooled to the boiling point of hydrogen must suddenly become a highly vacuous space. This was proved by the great difficulty of getting electric discharges to pass through specially prepared spectroscopic tubes when subjected to liquid hydrogen cooling, and from the fact that when the current did pass no lines of oxygen or nitrogen were seen, but only those of hydrogen, helium and neon. In order to separate these latter gases from air it was necessary to liquefy a quantity of air and to distil off the most volatile portion at as low a temperature as possible into a separate receiver placed in liquid hydrogen. In this way many spectroscopic tubes were filled with the uncondensable air gases and the results of their examination is recorded in a paper entitled "On the Spectra of the more Volatile Gases of Atmospheric Air, which are not Condensed at the Temperature of Liquid Hydrogen,"† by Professor Liveing and myself.

* 'Roy. Soc. Proc.,' vol. 64, 1898.

† 'Roy. Soc. Proc.,' vol. 67, 1900.

Some 2 years later I improved the method of separation of the volatile air gases. The process is fully described and illustrated in my paper on "Problems of the Atmosphere."* Its success depends upon the continuous direct liquefaction of air at atmospheric pressure combined with a device which enables the more volatile gases to be trapped and separated. In this way some 1/35,000th of the volume of the air liquefied is collected as a gaseous mixture, having the composition 38 per cent. of nitrogen, 4 per cent. of hydrogen, and 58 per cent. of mixed helium and neon. After sparking to remove the nitrogen and hydrogen, a gaseous mixture of helium and neon containing a little argon was obtained. This mixture had the composition of 16 per cent. helium and 84 per cent. neon. In both methods of treatment it will be noted the liquefaction of the air was the essential preliminary operation, to be supplemented in the one case by the use of liquid hydrogen, in the other by sparking to remove the nitrogen. The paper already communicated to the Royal Society, entitled "The Absorption and Thermal Evolution of Gases Occluded in Charcoal at Low Temperatures," in which the greatly increased power of occlusion possessed by charcoal at low temperatures is proved, suggested an inquiry into the limits of gaseous pressure reached by such means of condensation.

Fig. 1.



With this object a narrow tube CE, fig. 1, was sealed to an ordinary spectroscopic sparking tube AB, and at the end E an enlarged space was blown out capable of holding a few grammes of cocoanut charcoal. After the charcoal had been freed from gases by heating and exhaustion and the poles cleared by sparking during this operation, pure and dry gases like oxygen, nitrogen, air, carbonic oxide, hydrogen, neon and helium could be admitted at different pressures and the tube with its charcoal chamber attached sealed off.

On placing the charcoal end of the apparatus in liquid air the gas in each case was rapidly absorbed and the vacuum produced reached the phosphorescent stage in all cases with the exception of hydrogen, neon, and helium. A small Crookes's radiometer, full of air at atmospheric pressure, with charcoal tube attached, became quite active to heat radiation when the charcoal was cooled for half a minute in liquid air. To test the amount of exhaustion reached by the use of a given weight of cocoanut charcoal I sealed on a tube containing 30 grammes to a large electric discharge tube of 1300 c.c. capacity filled with air at atmospheric pressure. On cooling the charcoal receptacle in liquid air the pressure diminished to 50 mm. of mercury. Repeating the same experiment but starting with the tube initially at half an atmosphere, the exhaustion reached was now beyond the striæ stage. A further experiment starting with one-fourth of an atmosphere gave a vacuum through which no discharge passed.

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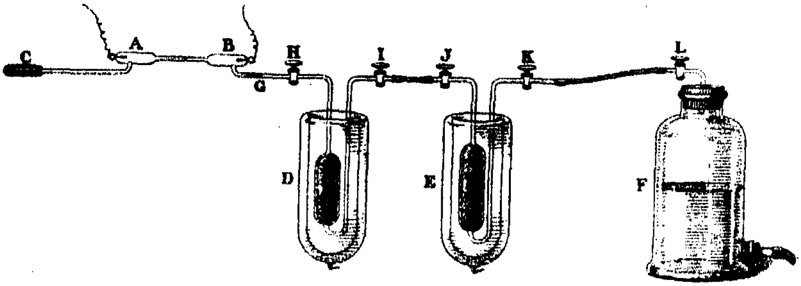
* 'Roy. Inst. Proc.,' 1902.

Finally, the 30 grammes of charcoal were replaced by only 1 gramme and the initial pressure was reduced to 3 mm. of mercury. Now the vacuum just reached the beginning of the phosphorescent stage. With hydrogen, either a pressure of gas less than that of the atmosphere had to be used at starting or a larger amount of charcoal employed in order to get a vacuum well up in the striæ stage. If, however, the liquid air was cooled to −210° C. by exhaustion, the tube just reached the beginning of phosphorescence round the cathodes.

With helium there was a very slight absorption, but neon did show something more appreciably. Spectroscopic observations made during the condensation of the gas in the charcoal showed the gradual disappearance of the characteristic spectrum of oxygen, nitrogen and air, as the high vacuum was reached and the discharge passed with great difficulty. In tubes of this kind filled at atmospheric pressure I could always see the F line of hydrogen and the neon yellow; but the helium was not seen with any definiteness. As the amount of neon in the air cannot well exceed 1/50,000th, the spectroscopic test is very delicate.

In order to bring in the helium lines it was necessary to concentrate the volume of air in the space of the sparking tube six or seven times. This was done by the use of an arrangement shown in fig. 2. A B is the sparking tube with its small charcoal bulb C attached, capable of being sealed off when required at G; and D and E are larger charcoal absorbers placed in vacuum tubes containing liquid air; the whole being attached to a graduated gas-holder containing air. A series of glass stop-cocks are attached at the points H, I, J and K in order to facilitate manipulation. In determining the volume of air required to bring in the helium lines only one charcoal absorber containing about 15 grammes of material was used. On allowing 200 c.c. of air from the gas holder to be sucked into the charcoal (which had been previously

Fig. 2.



exhausted along with the sparking tube), on opening the stop-cock H any residuary gas in D was swept into the sparking tube, which was then sealed off at G.

This tube gave the hydrogen lines C and F, the neon yellow, and some of the orange lines, along with the helium yellow and green quite distinct. With the residuary gas extracted from 1 litre of air I could see all the helium lines. On the positive pole the neon yellow and the green of helium were alone marked, while the negative pole gave both the neon and helium yellow lines along with the helium green and the F of hydrogen on the continuous spectrum. From this it would appear that the spectroscopic test for helium is as delicate as that for neon, and that 1/50,000th can be recognised. From 3 litres of air discharge tubes were obtained giving the neon and helium spectra associated with a brilliant ruddy glow discharge.

As 40—50 grammes of charcoal can absorb at the temperature of liquid air from 5—6 litres, it is easy to accumulate rapidly the uncondensed gases in considerable quantities for spectroscopic examination. For this purpose I found it convenient to use two charcoal condensers n circuit as represented in fig. 2. After the charcoal in the first one marked E was saturated, the stop-cock K was closed, while I and J were opened for a short time so as to allow the less condensable gas in E to be sucked into the second vessel of the same type D along with some portion of air. The charcoal condenser E was then taken out of the liquid air, and rapidly heated to 15° C. in order to expel the occluded air. It was thus in a condition to repeat the absorption. In this way 50 litres of air can be treated in a short time. Sparking tubes filled from the accumulated gases in D were very brilliant, showing the complete spectrum of the volatile constituents of air. It is hardly necessary to remark that after the little charcoal receptacle connected to each of the sparking tubes has been cooled and thus all traces of air absorbed, it can be sealed off, leaving the spectroscopic tubes intact. The complete spectroscopic study of the products must be left for further examination with Professor Liveing.

The method I have described will be equally applicable to the treatment of the gaseous products from minerals containing helium, hydrogen, etc., and also to the radium products of a similar kind. It seems even probable that the separation of the less volatile constituents in air may be improved by a slight modification in the mode of working. The behaviour of the gases from the Bath Springs has been examined. When the gas containing 1/1000th part of helium in what may be regarded as pure nitrogen is subjected to charcoal absorption exactly in the same way as the air was treated no high vacuum is reached. All the nitrogen and any other constituents disappear, and a spectrum of helium and hydrogen showing much less neon than exists in the volatile residue from atmospheric air is the result. A sample of argon made from Bath gas gave, when the argon was absorbed in charcoal, a gas residuum giving the helium and neon spectrum, and the same result follows the use of atmospheric argon. In the case, however, of the Bath gas argon the helium spectrum is the stronger, whereas with air argon the neon is the most pronounced.

In order to further test the method, the crude gases got by heating the mineral Fergusonite were examined. During the cooling of the charcoal the nitrogen and hydrogen spectra were marked, but in a short time nothing could be seen but the lines of hydrogen and helium.

Great interest will attach to the behaviour of helium, hydrogen and the most volatile part of air, when subjected to the action of charcoal cooled to the temperature of liquid hydrogen. The method promises to open up many avenues for future inquiry.

I am indebted to Mr. Robert Lennox, F.C.S., for efficient assistance in the conduct of the experiments, and Mr. J. W. Heath, F.C.S., has also helped me in the investigation.

"On the Action of Wood on a Photographic Plate in the Dark." By William J. Russell, Ph.D., F.R.S. Received May 28.—Read June 16, 1904.

(Abstract.)

[Plate 7.]

It has been shown in former papers that many substances are capable of acting on a photographic plate in the dark and producing a picture of themselves. Further investigation shows that this property belongs probably to all woods, some, however, being much more active than others.

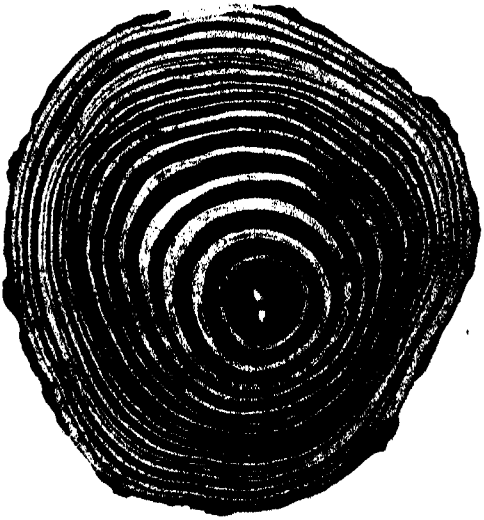
To obtain a picture the wood has to be in contact or at a little distance above the photographic plate, and has to remain there for times varying from ½ an hour to 18 hours, and to be at a temperature not higher than 55° C.

The wood of the conifers is very active, and gives pictures which are very definite. Fig. 1 is a picture of a section of a branch of a Scotch fir, and shows well the rings of spring and autumn growth. It is remarkable that the former are very active, producing in this picture the dark rings, and so with the other pictures, the part which is active in the original is dark in the picture. The rings seen in the wood are very sharp and strongly pronounced in the picture. If the action exerted on the plate be owing to the presence of hydrogen peroxide, as has been previously suggested, no doubt it is produced

by the resinous bodies present in the wood, but it is remarkable that there is no action from the dark autumn wood. Experiments described in the full paper show that resin exists in the dark rings, but apparently under such conditions that it cannot escape. Other members of the pine group have been experimented with and have been found to behave in the same way as the Scotch fir.

With the spruces the action on the plate is not so definite and well marked; the white wood is always active, but in some cases the dark rings are also active, and the pictures are not so sharp as with the firs. Larch wood gives a very interesting result, for the picture is the reverse of that of the Scotch fir, that is, the dark rings in the wood are the active rings and the light rings are inactive.

Fig. 1.



With regard to woods other than conifers, oak and beech are both active and give very good pictures, so also does acacia (*Robinia*), Spanish chestnut, and sycamore; on the other hand, ash, elm, horse chestnut, plane are comparatively but slightly active. In the full paper lists of woods are arranged according to their activity.

Many foreign woods are very active, but as the annual rings are often not well developed, the pictures they give are of a somewhat different character. The African black wood, rose-wood, cocobola, and many others are very active. Several of the foreign woods have a ring of white wood which is quite inactive.

Knots in a wood generally, but not always, give a good picture.

FIG. 1.

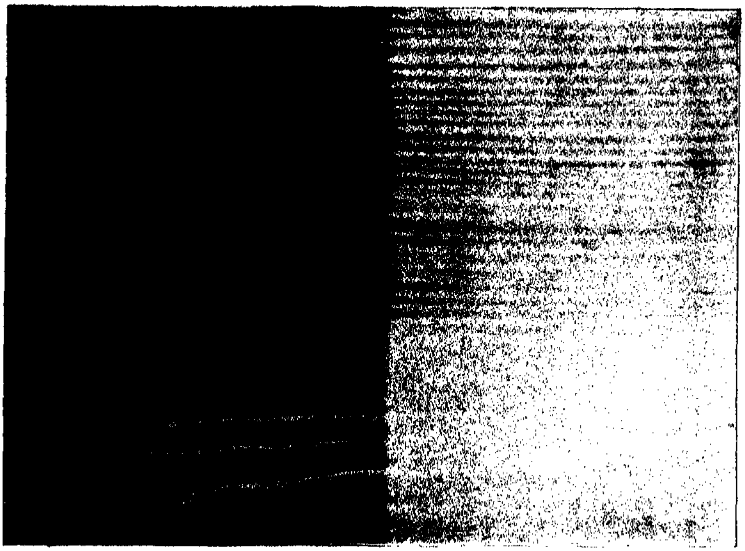
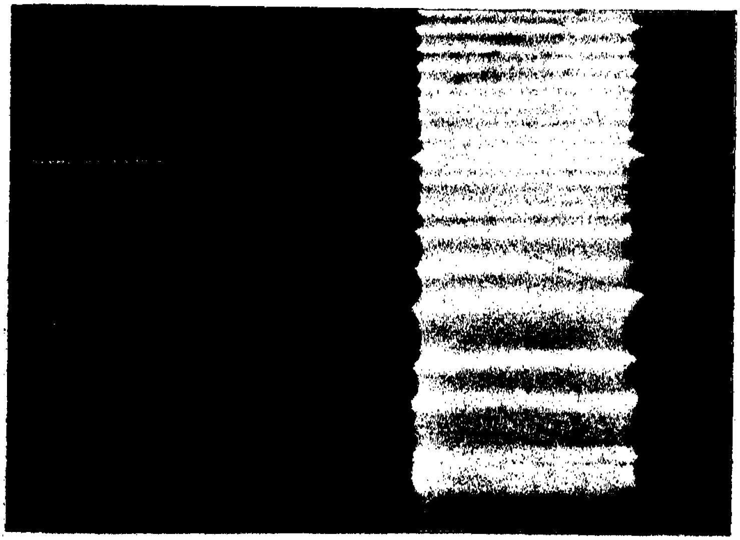


FIG. 2.



Some of the resin in immediate contact with the knot is in some cases but little active. The marked difference in properties of resins from different sources is described, and it is shown how difficult it is to remove it, so that the wood shall be no longer active. Boards that have been exposed to the air for a long time, an oak box a hundred or more years old, rotten wood from the stump of a tree, and even bog wood have all been found to be still active.

In addition to woods many different resins and allied bodies can, when used alone, be proved to be very active, some naturally much more so than others. Ordinary resins, Burgundy pitch, gum mastic, are very active, asphaltum, dragons blood much less so, but true gums such as gum senegal and gum arabic are entirely without action on a photographic plate.

In certain cases the picture obtained on the plate does not resemble the markings which are visible on the wood. With some woods this more commonly occurs than with others. That this picture is persistent in the wood is shown by fresh sections giving the same result. The true bark of a wood is apparently quite without action on a photographic plate, so is the internal pith of a plant.

There is another and a very interesting action, which occurs with wood, it is the great increase of activity which it exerts on a photographic plate after it has been exposed to a strong light. For instance, if a piece of deal be half covered by black paper or tin foil and be exposed for 5—10 minutes to bright sunlight, and then put up in the usual way with a photographic plate, it will give a dark picture where the light has fallen on the wood and only a very faint picture of the part which has been covered. This is shown in Plate 7, fig. 1. Even comparatively inactive woods such as elm and ivy after a short exposure to bright light give good and dark pictures. The action is not an indiscriminate darkening over the whole wood section, but an intensifying of the parts already active. This increase of activity by the action of light appears to occur with all woods. Artificial light, such as that from the electric arc, or from burning magnesium ribbon, act in the same way, so does even a faint light. A piece of wood put at a window for some hours will give a darker picture than a similar piece left in the middle of the room. This increase of power of a wood to produce a picture does not rapidly pass away. After 24 hours the action is visibly less, and decreases more rapidly at first than after some days, but it will be a fortnight or may be a month before the wood resumes its former condition. This action, like the former one, is entirely stopped by interposing the thinnest piece of glass or mica between the photographic plate and the active body. An inactive card painted with an alcoholic solution of resin, acts in the same way, and turpentine which has been exposed to a bright light acts more strongly on a photographic plate than it does when it has not been so exposed. Again, old printing which is now nearly inactive becomes much more active after exposure to sunlight. Bodies other than those which may contain resin or allied substances are not affected in this way by light, for instance, flour, sugar, porcelain ; metals are not rendered active by sunlight.

The next point was to ascertain which of the constituents of light was most active in producing these effects, and the first experiments were made by simply placing strips of different coloured glass on wood sections, exposing them to sunlight and afterwards putting them up with the photographic plate in the usual way. Pictures of the results are given in the paper. Red glass entirely prevented any increase in the activity of the wood, in fact, it acted in the same way as a band of black paper or tin foil would act, and a green glass acted much in the same way, but under a blue glass the activity of the wood was increased to much the same extent as under colourless glass or under no glass. Plate 7, fig. 2, shows what happens when a red glass and a white glass are placed upon it and exposed to sunlight. On the right of the figure there was no glass.

Further experiments were made by placing similar pieces of deal in light which had passed through different coloured solutions. Three double-cased bell jars were taken, one was charged with a solution of potassium bichromate, another with copper ammonium sulphate solution, and the third with pure water, and all were exposed to sunlight for 4 hours. The deal in the red light gave only a faint picture, that in the blue light a dark picture, and that with the pure water was only a slightly darker picture. Resin, guiacum, copal varnish, white oil paint and resin sized paper all acted in the same way and gave similar results.

The light from an arc lamp when passed through a red glass and allowed to fall on a wood section for 1½ hours produced no effect, but when the same light was passed through a blue glass and fell on a similar wood section for only 1 hour it produced a dark picture. With liquids this same increase of activity by the action of blue light is produced. Turpentine, which has been exposed to blue light, is more active than when in its ordinary condition.

"On the Production of a Specific Gastrotoxic Serum.—Preliminary Communication." By Charles Bolton, M.D., B.Sc., M.R.C.P., Research Scholar of the Grocers' Company. Communicated by Professor Sidney Martin, F.R.S. Received July 26, 1904.

(From the Pathological Laboratory, University College.)

[Plates 8 and 9.]

Within the last four or five years the study of cytotoxins has advanced rapidly, but this difficult subject is still involved in a vast amount of obscurity. Very few of the cytotoxins have been at all fully worked out, and, since it is becoming recognised that specificity is a term which should be applied to receptors and not to cells, the existence of many specific cytotoxins is doubted.

The present research was, therefore, undertaken from two points of view: (1) To add, if possible, any facts to our knowledge of cytotoxic action, (2) To throw some light upon the pathology of human gastric ulcer.

My first endeavour was to produce a hetero-gastrolytic serum by the injection of the mucous membrane of the stomach of the guinea-pig into the rabbit. Having succeeded in this direction, I then attempted to produce an iso-gastrolytic serum by the injection of the stomach cells of the rabbit into the rabbit and also of the stomach cells of the guinea-pig into the guinea-pig. In commencing the work I fully realised the difficulty of excluding bacterial infection and therefore have adopted strictly aseptic measures in the preparation of the mucous membrane for injection, making in addition bacteriological examinations of the injected animals.

Intraperitoneal injections are given, and in spite of the strictest precautions death occasionally results from bacterial infection; I have, however, succeeded in immunising 14 animals, and by injection of the serum obtained from them have produced lesions in the stomachs of over 50 animals, and have been able to show that the peritoneal cavity of immunised animals was sterile on bacteriological examination, whilst their blood serum was highly toxic for other animals.

The subject will be discussed under the following headings:—

(1.) Methods.
(2.) Effects of Injection of the Stomach Cells of the Guinea-pig into the Rabbit.
    (*a*) Symptoms following injection.
    (*b*) Changes in the rabbit's blood.
        Action of the serum on guinea-pig's cells *in vitro*.

- Action when injected into the guinea-pig.
    - Symptoms following injection.
    - Post-mortem lesions in guinea-pig.
- Nature of the gastrolytic serum.
    - Effects of heat.
    - Specificity of the serum.
    - Relation to hæmolysin.

(*c*) Changes in the rabbit's peritoneum.

(3.) Effects of Injection of the Stomach Cells of the Rabbit into the Rabbit.

- Changes in the rabbit's blood.
    - Action on injection into the rabbit.
    - Action on injection into the guinea-pig.
        - Effects of heat.
        - Effects of previous treatment with guinea-pig's stomach cells.
        - Effects of previous treatment with rabbit's stomach cells.

(4.) Effects of Injection of the Stomach Cells of the Guinea-pig into the Guinea-pig.

- Action on injection of the serum into the rabbit.

(5.) Action of Normal Rabbit's Serum on Injection into the Guinea-pig.

(6.) Action of Hæmolysin on Injection into the Guinea-pig.

(7.) Lesions in the Guinea-pig's Stomach due to Causes other than Hæmolysin or Gastrolysin.

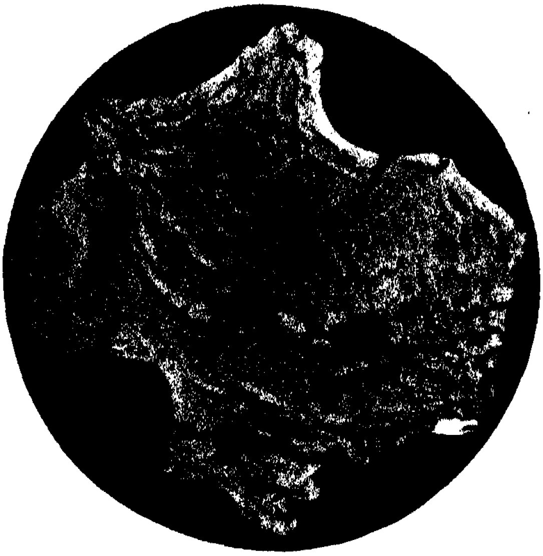
(8.) Conclusions.

(1.) METHODS.

Preparation of Mucous Membrane for Injection.—The instruments used for this purpose are a knife, a porcelain plate, a glass mortar, and a 10 c.c. syringe, all of which can be sterilized with the greatest ease.

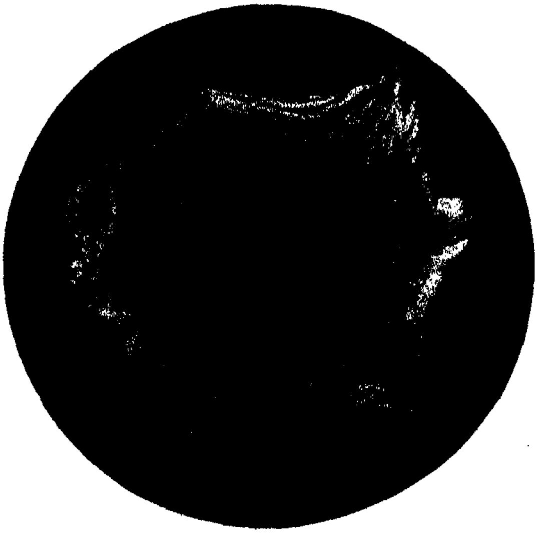
A guinea-pig which has been previously starved for about 24 hours, so that its stomach is empty, is killed with chloroform and the stomach at once cut out. It is opened and thoroughly washed in a stream of sterilized 0·86-per-cent. salt solution, all the adherent mucus being completely removed. The mucous membrane is then scraped off and ground up into an emulsion with salt solution, which is then injected into the peritoneal cavity of a rabbit. I have also used subcutaneous injections and have obtained the same results, but as suppuration is so liable to occur I have discarded them.

In two cases a fresh filtered extract of the mucous membrane was used for intraperitoneal injection. In one of these cases a 0·1-per-cent. hydrochloric acid solution and in the other a 0·4-per-cent. sodium bicarbonate solution was used for making the extract. The mucous



Stomach of Guinea-pig showing Two Ulcers. The animal received an injection of 12 c.c. of a weak gastrotoxic serum, and after 24 hours it was killed.

The serum was prepared by injecting a rabbit with fresh *extract* of guinea-pig's stomach cells.



Stomach of Guinea-pig showing a Large Ulcer situated on the Greater Curvature and several Smaller Ones. The animal received an injection of 12 c.c. of gastrotoxic serum, and was almost dead after 24 hours, when it was killed.

The serum in this case was prepared by injecting a rabbit with *rabbit's* stomach cells; in the other four cases *guinea-pig's* stomach was used for injection.

membrane was ground up in a glass mortar with a small quantity of sterilized sand in order to break up the cells, and an emulsion made with one of the above solutions. The emulsion was then filtered through a Pasteur-Chamberland filter and the resulting filtrate used for injection.

The effects obtained on injecting the serum of these two rabbits into guinea-pigs were exactly the same as those which resulted from injection of the serum of rabbits which had received injections of stomach cells.

Collection of Blood.—The blood is collected by opening a vessel of the ear, if possible an artery, having first shaved and disinfected the skin. In this way from 30–40 c.c. of blood can easily be obtained, without injury to the animal, especially if a flask of hot water be placed in contact with the ear to promote vaso-dilatation. The blood is whipped and centrifugalised.

The resulting serum is examined: (1) With regard to its action upon the stomach cells of the guinea-pig *in vitro*; (2) With regard to its action upon the guinea-pig's stomach when injected into the peritoneal cavity of that animal.

Examination in Vitro.—My plan has been to take a scraping from a fresh guinea-pig's stomach and carefully tease out the stomach glands in salt solution, separating them from the submucous and other tissue mixed with them. This is quite easily done by using the low power of a microscope or a dissecting lens. A portion of these glands is then placed in the serum to be examined, and a similar portion in normal rabbit's serum, the latter being used as a control.

The glands are examined at various periods of time up to 24 hours in the fresh condition, and also after fixing with osmic acid and staining with picro-carmine. In several cases small portions of the stomach wall were immersed in the serum for various periods of time and finally hardened, cut into sections in paraffin, and stained with hæmatoxylin and eosin.

Preparation for Microscopical Examination.—Patches of necrosed tissue with surrounding healthy mucous membrane were cut into a series of sections by the paraffin method. Eight or ten adjacent sections were selected from each row and fixed on slides, from six to twelve slides being thus obtained from each block. The sections were stained with hæmatoxylin and eosin. The stomachs of twenty animals have been investigated in this manner.

(2.) EFFECTS OF INJECTIONS OF THE STOMACH CELLS OF THE GUINEA-PIG INTO THE RABBIT.

(a) *Symptoms following Injection.*

The immediate symptoms in the rabbit are those of collapse, the temperature sinking to about 96°, the respiration being accelerated, and the animal prostrate. This is simply a vascular phenomenon due to the shock of injection, and the condition is soon recovered from, the animal subsequently taking its food well, and seeming to be quite healthy. Sometimes there is a fall in body weight, but this is by no means constant.

I have not found that any toxic symptoms follow the injection, and if the animal dies it is the result of bacterial infection.

(b) *Changes in the Rabbit's Blood.*

After four or five injections at intervals of 10 days, the blood serum of the rabbit is found to possess toxic properties.

Action in Vitro.—Contrary to the results of several observers, who have found that many tissue cells become dissolved in their corresponding cytotoxic sera, I have never been able to detect any difference whatever between the glands which had been exposed to the gastrolytic serum and those which had been similarly treated with normal rabbit's serum, although a marked effect was obtained on injecting the former serum into guinea-pigs.

In those cases in which the glands had been exposed for long periods of time to the two sera, each showed an equal degree of maceration in proportion to the time of exposure.

Action on Injection into Guinea-pigs.

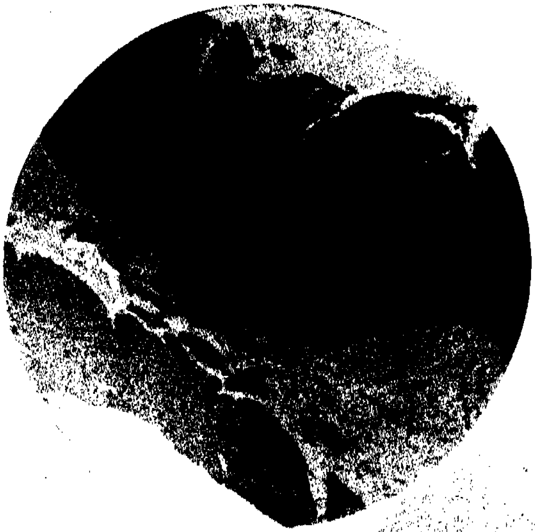
Symptoms following Injection.—In about half-an-hour after intraperitoneal injection of the serum the symptoms are well marked. The animal sits huddled up, with hair erect, and will not move. The temperature becomes subnormal.

If the dose of serum is small (1—5 c.c.), the animal will probably have quite recovered by the following day, but with large doses (10 c.c.) it becomes rapidly worse, and finally general twitchings commence, and the animal lies prostrate, death occurring generally within 24 hours.

In one case a guinea-pig weighing 280 grammes was killed by 5 c.c., and in another an animal weighing 140 grammes by 1 c.c., but, as a rule, the killing power of the smaller doses is uncertain. It may be stated that in most cases a dose of 10 c.c. is fatal for a guinea-pig weighing from 200—300 grammes within 24 hours.

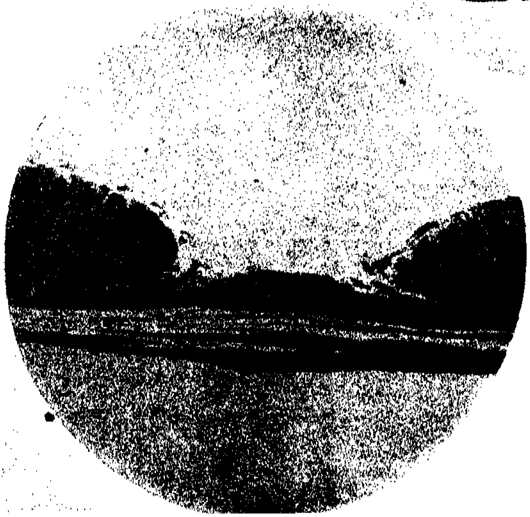
All guinea-pigs which are killed by the serum invariably show lesions in their stomachs, and a large proportion of those which receive small doses and recover show similar lesions. Speaking generally, the larger the dose administered, the greater is the effect upon the stomach. The lesions always occur during the first 24 hours after injection.

Macroscopic Appearance of Lesions in Stomach.—The lesions consist of patches of necrosis in the mucous membrane, and hæmorrhage. All the following lesions are described from cases which survived and



Section of Stomach Wall of Guinea-pig showing a large area of Necrosis in the Mucous Membrane. The animal received an injection of 4 c.c. of gastrotoxic serum, and was killed 24 hours afterwards.

Section of Stomach Wall of Guinea-pig at the edge of a Necrotic Patch. A blood-vessel containing normal red corpuscles can be seen in the patch. The animal received 5 c.c. of gastrotoxic serum, and was killed the next day.



Section of Stomach Wall of Guinea-pig showing an Ulcer. The animal received 10 c.c. of weak gastrotoxic serum, and was killed 48 *hours* afterwards.

were killed on the following day, *post-mortem* lesions being thus absolutely excluded.

The areas of necrosis appear in the form of black patches, round or irregular in shape, from the size of a pin's head to a large area, occupying a third or more of the surface of the stomach, and contrasting markedly with the surrounding mucous membrane which is normal. The black colour is due to altered blood pigment, a variable amount of which is usually found clinging with particles of food to the necrosed patches, from which it can be washed off, leaving the blackened and necrosed tissue plainly visible. This altered blood is present in very variable amount, sometimes being in considerable quantity, at other times scanty, with the necrosis greatly in excess.

The patches are found most commonly near or on one of the curvatures, but they may occur anywhere in the stomach. Their usual situation on the curvatures may be due to the fact that the main blood-vessels of the stomach run along the latter, and, therefore, these parts are the first to be exposed to the action of the toxin. Sometimes, also, the patches spread out into streaks, passing along the anterior and posterior walls of the stomach from the curvatures, as if they followed the distribution of the blood-vessels. In some places the necrosed tissue has disappeared, leaving ulcers with blackened edges and bases. After about 48 hours the black tissue apparently disappears, leaving a perfectly clean and sharply punched out ulcer.

Microscopic Appearance.—The necrosed patches are sharply marked off from the normal tissue, and do not extend beyond the muscularis mucosæ, the muscular coats and peritoneum being normal.

The cells of the glands in the necrosed patch, when they can be distinguished, are seen to be diffusely and very faintly stained by the eosin, their outlines are clouded, and they look shrunken; the nuclei are not stained, although towards the margin of the patch they can just be distinguished.

In a small patch, which is apparently just commencing, the cells, both oxyntic and central, have the above appearances, whilst the interstitial connective tissue cells take the stain well, and show up by contrast. In a farther advanced stage the whole patch is diffusely stained a faint pink colour or totally unstained, and the gland cells are irregularly arranged more or less in columns, but no definite idea of what structure had preceded this patch can be made out. A certain amount of altered blood pigment in the form of scattered brownish granules can be seen, but, as a rule, the necrosed tissue is singularly free from blood.

Towards the edge of the patch the normal tissue contains a few necrosed cells, and the edges and base are infiltrated with leucocytes. In many sections the bases of the glands do not appear to be so disintegrated as the inner ends. Sometimes the patch looks like a brownish coagulated mass in which no structure can be made out; at other times strands of interstitial tissue alone can be seen, the gland cells having completely disappeared.

A definite ulcer is formed by the gradual disappearance of the necrosed tissue. The blood in the vessels is generally normal, and frequently so when they are situated inside the necrosed patch. In the other cases it is apparently hæmolysed, and in one case a large mass of hæmolysed blood was seen infiltrating the submucous tissue.

The remaining portions of the alimentary canal have invariably been found to be normal, and no lesion has been detected in any other organ of the body. The primary lesion in this necrotic process is, I think, undoubtedly the result of a direct action of the gastrotoxin upon the gland cells, with a subsequent digestion of this tissue by the gastric juice, the black colour being due to the action of the gastric juice upon the blood which is contained in the necrosed patch.

As no change as a result of the action of the gastrotoxin *in vitro* can be made out, the questions must be raised whether the serum can produce necrosis when it attacks a cell having its normal lymph supply and normal connections in the body, or whether it only produces a devitalisation of the cell, thus allowing of its digestion by the gastric juice, which in this way renders the lesions visible. Previous work upon other cytotoxins does not settle the question one way or the other, because in some cases necrosis has been stated to occur, as in the liver, whilst in other cases no change has been found whatever, as in the pancreas and suprarenal body.

Hæmolysis undoubtedly occurs to a variable extent in different cases, and may account for a part of the hæmorrhage, though usually no laking of the blood can be seen in the vessels of the stomach.

In my opinion the lesions are not primarily due to hæmorrhage, because the appearance of a hæmorrhagic erosion is different from the necrotic patches described above; there are no hæmorrhages to be seen in the mucous membrane of the stomach, such as one would expect, and none occur in any other organ of the body. There is, moreover, no reason to suppose that the capillary endothelium of the stomach is sufficiently special in constitution to evoke the formation of a specific endotheliolysin.

Infarction can also be excluded by the limitation of the lesion to the mucous membrane, by the very irregular shape of the large patches, which sometimes contain islands of normal tissue, and by the fact that no clots can be found in the vessels either of the stomach or any other organ.

In some cases where the hæmolytic factor is more than usually in evidence, there is no doubt that some of the erosions may be the result of such a factor, but in my experience these erosions present quite a different appearance from the necrotic patches described above, the tissue being obviously broken up by the blood. It is a remarkable fact that evidence of hæmolysis should be found in the stomach and not in the other organs of the body in these cases.

Nature of the Gastrolytic Serum.—The experiments which I have made indicate that the gastrotoxin consists of an "immune body" or "amboceptor," which is newly formed in the blood as a result of the injection of the stomach cells, and a "complement" which is contained in the normal blood serum.

Effects of Heat.—If the serum be heated to from 55—60° C. for 1 hour its action on injection into the guinea-pig is destroyed, although the control animals which are injected with unheated serum show extensive necrosis of the stomach. On the other hand, if heated serum be added to an equal volume of normal rabbit's serum, the action is restored when the mixture is injected into the guinea-pig, but the resulting lesions are not quite so extensive as in the case of the unheated serum.

The guinea-pig's complement does not appear to possess a haptophoric affinity corresponding to the complementophile affinity of the gastrolytic amboceptor. The action of a hæmolysin, formed by injecting a rabbit with guinea-pig's corpuscles, is, on the contrary, not destroyed by heat; this agrees with the test-tube phenomenon that guinea-pig's normal serum will reactivate the heated hæmolytic serum of a rabbit.

Specificity of the Gastrotoxin.—This property has been tested by mixing various cells with gastrolytic serum previous to its injection into the guinea-pig, in order to determine whether guinea-pig's stomach cells alone or whether any other cells could extract the amboceptor.

The cells were allowed to remain in contact with the serum for 1 hour at laboratory temperature, and were then centrifugalised off and the supernatant serum injected. Control animals were in each case injected with untreated serum.

Admixture of Guinea-pig's Stomach Cells.—Whether the stomach cells are washed free from blood or not they anchor the amboceptor and carry it down on centrifugalisation, with the result that the serum is rendered inactive on injection into the animal.

Guinea-pig's Liver Cells.—The liver cells washed free from blood fail to extract the amboceptor, and necrosis of the stomach results when the serum is injected.

Guinea-pig's Red Blood Corpuscles.—The experiment was done in two ways, and in each case the red corpuscles failed to extract the amboceptor. In one case the gastrolytic serum was cooled to 0° C. and mixed with the corpuscles; the mixture being kept at 0° C. for 1 hour, was afterwards centrifugalised. In another case the serum was heated to 60° C. for an hour; excess of red corpuscles was then added to it and the mixture kept at laboratory temperature for 1 hour. The corpuscles were then centrifugalised off and normal rabbit's serum added to the supernatant fluid. On injecting this mixture into a guinea-pig stomach lesions resulted.

It was proved that the corpuscles had extracted the hæmolytic factor, because on adding to the heated serum some guinea-pig's corpuscles and normal guinea-pig's serum, complete laking resulted, whereas on adding the corpuscles and normal serum to the gastrolytic serum, which had been treated with red corpuscles previously, no laking or only a slight discoloration of the serum immediately above the deposited corpuscles was visible after 24 hours.

Rabbit's Stomach Cells.—These cells also failed to extract the gastrolytic amboceptor. As will be seen later, this experiment stands on a different footing from the last three, and the fact of the cells failing to extract the amboceptor does not prove that they do not possess an affinity for such amboceptor.

Relation to Hæmolysis.—The specificity of the gastrotoxin was also tested by immunising a rabbit against washed guinea-pig's stomach. The washing was carried out by passing a cannula into the thoracic aorta, cutting the inferior vena cava above the diaphragm, and then allowing a stream of sterilised salt solution to flow through the cannula until the blood was completely washed out of all the abdominal organs. This experiment is quite easily accomplished.

The serum of this rabbit showed a great increase in its hæmolytic power after it had received three injections of stomach cells, and the serum on injection into a guinea-pig caused necrosis of the stomach. This experiment affords confirmation of the fact, which was first demonstrated in the case of spermatozoa by Moxter and in the case of ciliated epithelium by Von Dungern, that different kinds of cells may contain similar receptors.

In the present instance the gastric cells not only contain specific receptors peculiar to themselves, but they also contain receptors similar to those of red blood corpuscles. Whether other cells of the body may contain receptors similar to those which I have stated as being peculiar to the gastric cells the above experiments do not conclusively prove. So far as they go the experiments prove that, at any rate if present in other cells, the gastric receptors are not so abundant in them as in the gastric cells themselves; other cells may contain a few of those receptors, but not sufficient to extract all the immune body contained in the serum.

At any rate, in the present state of our knowledge, these experiments tend to show that the gastrotoxin not only contains a specific amboceptor, which has an affinity for the receptors peculiar to the gastric cells, but also an amboceptor having an affinity for the receptors which the gastric cell possesses in common with red blood corpuscles. The term "specificity" used strictly should not, therefore, be applied to the gastrolytic serum itself, but to that part of it which has a specific affinity for the receptors peculiar to the gastric cells.

(c) *Changes in the Rabbit's Peritoneum.*

If an animal which has received several injections be killed a few weeks after the last one, the peritoneum will show slight opacity and thickening in various places, or slight adhesions between adjacent coils of intestine may be seen, or small pedunculated nodules may be present. The remaining portions of the peritoneum are quite normal.

The nodules on section are found to be composed of concentric layers of fibrous tissue, generally inclosing within them a group of epithelioid cells, and occasionally a giant cell, the nuclei of which are arranged in the centre. Whether these nodules are formed during the absorption of the stomach cells, as they were not seen in the cases in which an extract of stomach cells was injected, or owing to the presence of isolated bacteria, I am not prepared to state. At any rate, a bacteriological examination of such a peritoneum shows that it is sterile.

A few days after an injection the peritoneum is in places smeared over with a thin layer of cheesy material, and masses of the same material may exist between the coils of the intestine; elsewhere the peritoneum is normal. Microscopically, this substance consists of proliferated peritoneal epithelium and exuded leucocytes. This substance is also sterile on cultivation.

Last year, after I had commenced the present research, a paper was published by Théohari and Babès on a gastrotoxin. This is the only paper, so far as I am aware, dealing with the subject, and, as the authors obtained different results from mine, I will here briefly enumerate them.

The mucous membrane of the dog's stomach was subcutaneously injected into the goat, and, on injection of the goat's serum into the dog, they obtained the following results:—

(1) Pronounced hypersecretion of the stomach cells in the case of the weak gastrotoxic serum.

(2) Rapid death, with intense hyperæmia of the stomach, and especially of the intestine in the case of the stronger serum.

(3) In small doses, excitation of gastro-intestinal peristalsis and intestinal hæmorrhage. The chief cells in the stomach show functional changes; the marginal cells show degenerative changes. No change in the pyloric region of the stomach or the large intestine.

(4) The serum, specific against the peptic region of the dog's stomach, produces, moreover, material alterations in the small intestine, whilst the large intestine remains normal.

(3.) EFFECTS OF INJECTION OF THE STOMACH CELLS OF THE RABBIT INTO THE RABBIT.

The same initial symptoms, and the same changes in the rabbit's peritoneum, are observed as in the case of injection of guinea-pig's stomach cells.

Changes in the Rabbit's Blood.—I have been unable to produce any stomach lesion, or demonstrate any toxic action, on injecting the serum into a rabbit.

Action on Injection into the Guinea-pig.—That the blood has acquired toxic properties, however, I have shown by injecting the serum into guinea-pigs. Identical lesions are obtained by such injections with those described above.

Effects of Heat.—My experiments so far tend to show that, on heating the serum to 50—60° C. for 1 hour, the action is destroyed if the serum has only a low toxicity, but that some action may remain in the case of the more toxic sera. According to these results, the guinea-pig serum may to some extent complement this amboceptor.

Effects of Previous Treatment with Guinea-pig's Stomach Cells.—The stomach cells extract the amboceptor, and render the serum inactive, as described in dealing with the serum obtained by injecting the rabbit with guinea-pig's cells.

Effects of Previous Treatment with Rabbit's Stomach Cells.—In this case the rabbit's stomach cells entirely fail to anchor the amboceptor, and, on injecting the serum thus treated into a guinea-pig, necrosis of the stomach results. The same result was seen in the serum of rabbits immunised with guinea-pig's cells.

From these experiments I think it may be inferred that the rabbit can produce a gastrolytic serum when rabbit's stomach cells are injected into its body. And also, that the immune body thus produced has two cytophilic affinities: (1) for the receptors of the rabbit's stomach cells, since it is formed in response to their injection; (2) for the guinea-pig's stomach cells, since it causes necrosis of them.

Another alternative would be to assume that two separate immune bodies are formed. Whichever of these two views be accepted, the conclusion follows that the failure of the rabbit's stomach cells to anchor the immune body for which they have an affinity points to the hypothesis that this junction is prevented by the interposition of an anti-immune body, this anti-immune body having presumably been formed by the rabbit to protect its own stomach and prevent autolysis.

If we accept the view that two separate immune bodies are formed, we must also conclude that the rabbit's stomach cell has receptors similar to the guinea-pig's, as well as those peculiar to itself; this view presents the difficulty that we cannot explain why the guinea-pig's cells should anchor the immune body, whilst the rabbit's cells will not. On the other hand, if we accept the view that there is one immune body only, but that it has two cytophilic affinities, that corresponding to the rabbit's receptor being saturated by an anti-immune body, but that corresponding to the guinea-pig's receptor being free, the above difficulty vanishes.

(4.) EFFECTS OF INJECTION OF THE STOMACH CELLS OF THE GUINEA-PIG INTO THE GUINEA-PIG.

The serum in this case was shown to be toxic by injecting it into a rabbit, when typical necrosis resulted. A difficulty encountered here is due to the fact that a sufficient amount of blood cannot be obtained from the guinea-pig in order to inject an amount corresponding to the weight of the rabbit which would lead to a result as marked as that obtained in the guinea-pig's stomachs described above.

This experiment also shows that when an animal absorbs cells which have been taken from the body of an identical animal its blood becomes toxic.

(5.) ACTION OF NORMAL RABBIT'S SERUM ON THE GUINEA-PIG.

The blood serum of the rabbit is to some extent hæmolytic for the guinea-pig's red corpuscles. On injection of the serum into a guinea-pig, even in large does (20 c.c.), no lesions are found in the stomach or alimentary canal such as result from hæmolysis. In one case a patch of engorged vessels was seen in the stomach, but no hæmorrhage or necrosis was to be observed.

(6.) ACTION OF STRONGLY HÆMOLYTIC SERUM.

After a rabbit has received several injections of guinea-pig's red corpuscles a marked effect is observed on injecting the rabbit's blood serum into a guinea-pig. The lesions produced consist of hæmorrhage with distortion and solution of the blood corpuscles. The hæmorrhages are best seen in the alimentary canal. They occur in the stomach and lead to erosions of the mucous membrane as a secondary consequence, but patches of necrosis in the mucous membrane are not seen. Hæmorrhages are also seen in the lymphatic follicles of the intestine, especially the colon. There is intense engorgement of the organs and hæmorrhages may occur all over the mesentery.

Effects of Heat.—On heating the hæmolytic serum to 50—60° C. for an hour, its action is not destroyed, the guinea-pig's serum being able to complement the hæmolytic amboceptor. The differences between the action of a hæmolytic and a gastrotoxic serum are thus seen to be very considerable.

(7.) LESIONS IN THE GUINEA-PIG'S STOMACH DUE TO CAUSES OTHER THAN HÆMOLYSIS OR GASTROLYSIS ARE OCCASIONALLY SEEN.

If the stomachs of a large number of normal guinea-pigs are examined regularly, there may occasionally be seen patches of congestion in the mucous membrane; sometimes hæmorrhages are present, and in two cases I have found ulcers. What the pathology of this condition is does not seem quite clear, but probably the ulcers are of hæmorrhagic origin.

In two cases of septic peritonitis in guinea-pigs I have found hæmorrhage into the stomach and small intestine. On microscopic examination they present a very typical appearance, the blood being extravasated into the substance of the mucous membrane, and exhibiting quite a different appearance from patches of necrosis.

(8.) CONCLUSIONS.

(*a.*) On either intraperitoneal or subcutaneous injection of the stomach cells (or a fresh extract of them) of the guinea-pig into the rabbit, the blood serum of the latter becomes highly toxic for guinea-pigs.

(*b.*) The serum leads to death on injection into the guinea-pig and causes necrosis of the mucous membrane of the stomach, leading to ulceration and hæmorrhage.

(*c.*) The toxin contained in the serum consists of at least two factors: (1) A specific Gastrolysin, which leads to necrosis; (2) A Hæmolysin which assists in producing hæmorrhage. The hæmolytic factor can be removed, leaving the gastrolytic, which still produces stomach lesions.

(*d.*) The gastrolysin is a specific cytotoxin and consists of an immune body and a complement.

(*e.*) The gastrolysin does not visibly affect the cells *in vitro*.

(*f.*) The gastrolysin does not produce necrosis in the stomach of the animal which has elaborated it, possibly owing to the concomitant formation of an anti-immune body.

(*g.*) By injection of the stomach cells of the rabbit into the rabbit a gastrolysin is formed which causes necrosis in the guinea-pig's stomach; it therefore possesses at least two cytophilic affinities.

(*h.*) By injection of the stomach cells of the guinea-pig into the guinea-pig a gastrolysin is formed which causes necrosis in the stomach of the rabbit; this gastrolysin is probably of a similar nature as the preceding.

(*k.*) The importance of the above conclusions with regard to the pathology of human gastric ulcer lies in the fact that an animal can elaborate in its blood by the absorption of the cells of a similar animal, and therefore presumably of its own, a toxin which would cause necrosis in the mucous membrane of its own stomach were it not for some deterring influence, probably the concomitant formation of an anti-immune body.

REFERENCES.

Théohari et Babès.	"Note sur une Gastrotoxine," 'Compt. rend. de la Soc. de Biol.,' 1903, No. 13.
Von Dungern	'Munich Med. Wochenschrift,' 1899.
Moxter..........	'Deutsche Med. Wochenschrift,' 1900.

"On the Action exerted upon the *Staphylococcus pyogenes* by Human Blood Fluids, and on the Elaboration of Protective Elements in the Human Organism in Response to Inoculations of a Staphylococcus Vaccine."

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(From the Pathological Laboratory of St. Mary's Hospital, London, W.)

The subject matter with which we have here to deal may be distributed under the following headings:—

(1) Determination of the nature of the action which is exerted upon the *Staphylococcus pyogenes* by normal human blood fluids, and by the blood fluids of patients who have been inoculated with a staphylococcus vaccine.

(2) Comparison of the phagocytic power of the subjects of staphylococcus invasion with the phagocytic power of normal individuals.

(3) Distribution in the infected organism of the opsonins which here come into consideration.

(4) Determination of the question as to whether the opsonins are present in the blood of the infant at birth.

(5) Determination of the course of the reaction of immunisation which supervenes upon the inoculation of a staphylococcus vaccine.

(1) *Nature of the Action which is exerted upon the* Staphylococcus pyogenes *by Normal Blood Fluids, and by the Blood Fluids of Patients Inoculated with a Staphylococcus Vaccine.*

Bactericidal Action.—It was shown in the course of the classical researches on the bactericidal power of the blood which were conducted by Nuttall* in Flügge's laboratory, that the staphylococcus offers resistance to the bactericidal action of the blood fluids. Two years afterwards the observations of Nuttall, which had reference to the blood of animals, were extended by Stern† to human blood. The methods employed by Nuttall and Stern alike did not, however, permit of a comparatively small bactericidal action being distinguished from a complete absence of bactericidal action.

The question as to how far the staphylococcus offers resistance to the bactericidal action of human blood was reinvestigated by one of us, the results being published (*a*) in a paper dealing with anti-staphylococcus inoculations‡, and (*b*) in a paper written in conjunction with Captain F. Windsor, I.M.S.,§ on the bactericidal action exerted by human blood upon a variety of pathogenic micro-organisms. It was established in the researches here in question, which were conducted with the more delicate methods of investigation set forth in the 'Proceedings of the Royal Society'‖ and in the 'Lancet'¶ respectively, (*a*) that normal human blood does not exert upon the staphylococcus any bactericidal action whatever, and (*b*) that anti-staphylococcus inoculations do not lead to a development of any bactericidal power in the blood.**

Opsonic Action.—It having become evident in the course of these researches that the effect of anti-staphylococcus inoculation is not to be found in a development of bactericidal properties in the blood fluids, attention was directed to the measurement of the phagocytic power of the blood. Taking to aid the method of phagocytic estimation devised by Major W. B. Leishman, R.A.M.C., it was ascertained that successful immunisation against staphylococcus goes in every case hand in hand with the acquirement of increased phagocytic power.

Certain difficulties having suggested themselves in connection with the attribution of this result to a "training" of the white blood corpuscles we addressed ourselves to a further investigation of the phenomena of phagocytosis.

In the course of this investigation†† it became clear that phagocytosis of bacteria is dependent upon an effect exerted upon the bacteria by the blood fluids. We spoke of this effect as an opsonic effect.

In a second research,‡‡ in which we extended our previous observations, on the opsonic power of the blood fluids, we showed that the increased phagocytic effect which is obtained with the blood of successfully immunised persons is attributable not to any modification induced in the leucocytes, but to an increased opsonic power in the blood fluids. Conclusive evidence of this was obtained by separating, in the case of two bloods of conspicuously different phagocytic power in each case, the blood fluids from the corpuscular elements and then effecting an interchange of the blood fluids. The leucocytes of the successfully immunised patient exhibited under these circumstances the smaller phagocytic action characteristic of the blood of the normal individual who served as a control, while the leucocytes of the normal individual exhibited the increased phagocytic action characteristic of the blood of the successfully immunised patient.

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* Nuttall, 'Zeitschrift f. Hygiene,' 1888, vol. 4.

† Stern, 'Verhandlungen des IX Congresses f. Innere Medicin,' 1890.

‡ Wright, 'Lancet,' March 29, 1902.

§ Wright and Windsor, 'Journal of Hygiene,' vol. 2, No. 4, March, 1902.

‖ Wright, 'Roy. Soc. Proc.,' vol. 71, 1902.

¶ Wright, 'Lancet,' December 1, 1900, and March 2, 1901.

** *Vide* 'Journal of Hygiene' (*loc. cit.*), Tables VII and VIII.

†† Wright and Douglas, 'Roy. Soc. Proc.,' 1903, vol. 72.

‡‡ Wright and Douglas, 'Roy. Soc. Proc.,' 1904, vol. 73.

The witness of the experiment just referred to, and of a previous experiment incorporated in our first paper, is confirmed by similar results obtained in connection with the tubercle bacillus. See pp. 164—165.

Agglutinating Action.—Normal human serum does not exert any characteristic agglutinating action upon the staphylococcus. Such agglutination as is obtained is not very sensibly increased under the influence of staphylococcus inoculations.

(2) *Comparison of the Phagocytic Power of the Subjects of Staphylococcus Invasion with the Phagocytic Power of Normal Persons.*

It is clear from what has been said above that the essential change which takes place in human blood, as a result of the inoculation of staphylococcus cultures, is an increase in the phagocytic power, dependent upon an increase of the opsonic elements in the blood.

Further evidence of the essential importance of the phagocytic and opsonic power in connection with resistance to staphylococcus invasions is obtained by contrasting the phagocytic power of the subjects of staphylococcus invasion with that of normal individuals.

Our observations on this subject were made in some instances by comparing the phagocytic power of the decalcified blood of the patient with the phagocytic power of the decalcified blood of a normal person. More frequently we employed in our experiments respectively, the patient's serum and the serum of a normal person in each case in association with the washed corpuscles derived from a normal man.

The results of our observations are tabulated below :—

Table showing the Ratio in which the Phagocytic or Opsonic Power of the Patient's Blood stood in each case to the Phagocytic or Opsonic Power of the Normal Individual who furnished the Control Blood.

(The phagocytic power of the control blood is taken in each case as unity.)

Initials of patient.	Form of staphylococcus invasion.	Phagocytic or opsonic index.
E. G.	Furunculosis	0·48
F. F.	Sycosis	0·49
J. E.	Acne	0·64
J. H.	Furunculosis	0·87
W. B.	Acne	0·55
E. H.	„	0·82
W. H.	Furunculosis	0·79
R. G.	„	0·7
G. L.	Acne and sycosis	0·74
S. O.	Furunculosis	0·87
W. L.	„	0·88
W. P.	„	0·39
S. F.	Very aggravated sycosis.	0·1
E. F. D.	Acne	0·78
D. C.	Sycosis	0·8
J. M.	Acne	0·48
W. M.	Sycosis	0·37
E. P.	Acne	0·6
M. S.	Pustular affection of lips	0·6
F. V.	Repeated septic-infection	0·47

In view of these observations and of the fact that we have not come across any instance of the association of a normal phagocytic power with a staphylococcus infection, the conclusion would seem justified that a low phagocytic power and staphylococcus infection are related to each other by some fact of causation. While it is *à priori* possible that the diminished phagocytic power which characterises those infected by the staphylococcus might be the result of the staphylococcus invasion, it is infinitely more probable, in view of the entire absence of clinical symptoms in the slighter cases of staphylococcus infection, that it is the defective phagocytic power of the patient which furnishes to the staphylococcus which is normally present upon the surface of the body the opportunity for invading the skin.

It is shown elsewhere (see p. 166) that a similar problem arises in connection with the circumstance that a low phagocytic power, with respect to the tubercle bacillus, is generally found in association with tubercular infection.

(3) *On the Distribution of Opsonins in the Infected Organism.*

It is a fundamentally important but unappreciated fact in connection with bacterial infections that the *bacteriotropic pressure*—we designate by this term the mass effect exerted upon the invading bacteria by the protective substances contained in the blood fluids—does not stand at the same level in every part of the infected organism.

One of us has, in conjunction with Captain George Lamb, I.M.S.,* demonstrated in the case of patients who had succumbed respectively to typhoid and Malta fever that the amount of agglutinins in the splenic pulp is invariably less,† in some instances over 200 times less, than in the circulating blood. It was further shown in the paper in question that there was a similar difference as between the fluid obtained from the typhoid spots and the fluid of the circulating blood. Captain Lamb‡ gave a further extension to these observations by demonstrating, in the case of monkeys examined immediately after the crisis of spirillum fever, that the splenic pulp (where the spirilla still survive after they have disappeared from the circulation) is much poorer in bactericidal and bacteriolytic substances than the circulating blood.

It is shown by these observations that the *Bacillus typhosus*, the *Micrococcus melitensis* and the *Spirillum Obermeyeri*, respectively multiply, or, as the case may be, maintain their existence, within the infected organism in regions of low bacteriotropic pressure. We may legitimately assume that the lowered bacteriotropic pressure in the nidus, where the micro-organisms are cultivating themselves, results from a retarded replacement of protective substances which are removed from the body fluids where these come into contact with bacteria.

Influenced by the results of the observations which have been just set out, we have addressed ourselves to the task of investigating the distribution of the opsonins in the case where the human organism is invaded by the staphylococcus. With this intent we have instituted comparisons between the serum obtained from the circulating blood and the fluid obtained by centrifugalisation from pus. It will be seen from the observations set forth below that what has been shown to hold true with respect to the distribution of agglutinins and bactericidal and bacteriolytic substances respectively in the bacterial infections before-mentioned, holds true also in the case of the opsonins in the case of staphylococcic infection. In view of this fact, and of the similar facts which we set out elsewhere in connection with tubercular infection (see pp. 167—169), it may be enunciated as a proposition of general application that the invading micro-organisms cultivate themselves in the organism in regions of lowered bacteriotropic pressure.

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* Wright and Lamb, 'Lancet,' December 23, 1898.

† This observation so far as it applies to typhoid had been anticipated by Paul Courmont, 'Soc. de Biologie,' February 20 and March 28, 1897.

‡ Lamb, 'Scientific Memoirs by Officers of the Medical and Sanitary Departments of the Government of India,' vol. 12, pp. 96, *et seq.*

Case 1.

13.4.04. Patient with an alveolar abscess pointing on the cheek. Pus gives a pure culture of staphylococcus.

A.

Patient's serum	2 vols.
A. E. W.'s washed corpuscles	2 ,,
Staphylococcus emulsion	1 vol.

Phagocytic index* (average of 20 P.W.B.C.), **30·3.**

B.

Supernatant fluid from pus	2 vols.
A. E. W.'s washed corpuscles	2 ,,
Staphylococcus emulsion	1 vol.

Phagocytic index (average of 20 P.W.B.C.), **5·1.**

Ratio of opsonic index of serum to opsonic index of supernatant fluid from pus, 1 : 0·17.

15.4.04. Patient has had fomentations applied to cheek since abscess was opened on 13.4.04. Abscess rapidly healing.

A.

Patient's serum	2 vols.
A. E. W.'s washed corpuscles	2 ,,
Staphylococcus emulsion	1 vol.

Phagocytic index (average of 20 P.W.B.C.), **10·05.**

B

Supernatant fluid from pus	2 vols.
A. E. W.'s washed corpuscles	2 ,,
Staphylococcus emulsion	1 vol.

Phagocytic index (average of 20 P.W.B.C.), **10·1.**

Ratio of opsonic index of serum to opsonic index of supernatant fluid of pus, 1 : 1.

Case 2.

Patient with patellar abscess. Pus from abscess furnishes a pure growth of streptococcus.

A.

Patient's serum	2 vols.
A. E. W.'s washed corpuscles	2 ,,
Staphylococcus emulsion	1 vol.

Phagocytic index (average of 20 P.W.B.C.), **14·2.**

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* The phagocytic index was here, as elsewhere, determined by counting the number of bacteria ingested in the specified number of polynuclear leucocytes after digesting together in a capillary tube for 15 mins. at 37° C. the serum, corpuscles, and bacterial suspension.

B.

Supernatant fluid of pus	2 vols.
A. E. W.'s washed corpuscles	2 ,,
Staphylococcus emulsion	1 vol.

Phagocytic index (average of 40 P.W.B.C.), **1·25.**

Ratio of opsonic index of serum to opsonic index of supernatant fluid of pus, 1 : 0·09.

(4) *Determination of the Question as to whether the Opsonins which come into Consideration in Connection with the Protection of the Organism against Staphylococcus Invasion are present in the Blood of the Infant at Birth.*

Opportunity offering, we have thought it worth while to determine whether the protective substances which come into consideration in connection with the Staphylococcus pyogenes are present in the blood at birth. For this purpose we have made a series of comparative estimations of the opsonic power of the blood of child and mother, employing for this purpose respectively placental blood and blood drawn off directly from the mother immediately after the completion of parturition. We are indebted to Messrs. B. H. Spilsbury and J. Freeman for the collection of the bloods. The observations we have made are as follows :—

Observations.

Blood drawn off, in the case of the mother, from the finger; in the case of the child, from the umbilical cord.

No. 1.

A.

Mother's serum	3 vols.
A. E. W.'s washed corpuscles	3 ,,
Staphylococcus emulsion	1 vol.

Phagocytic index (average of 20 P.W.B.C.), **15·1.**

B.

Child's serum	3 vols.
A. E. W.'s washed corpuscles	3 ,,
Staphylococcus emulsion	1 vol.

Phagocytic index (average of 20 P.W.B.C.), **16·5.**

No. 2.

A.

Mother's serum	2 vols.
A. E. W.'s washed corpuscles	2 ,,
Staphylococcus emulsion	1 vol.

Phagocytic index (average of 20 P.W.B.C.), **12·65.**

B.

Child's serum..........	2 vols.
A. E. W.'s washed corpuscles ...	2 „
Staphylococcus emulsion	1 vol.

Phagocytic index (average of 20 P.W.B.C.), 12·25.

(5) *Determination of the Course of the Reaction of Immunisation obtained in response to Inoculations of a Staphylococcus Vaccine.*

We have in a very considerable number of cases plotted out by the aid of the phagocytic method the course of the reaction of immunisation which occurs in response to inoculations of a staphylococcus vaccine.

A preliminary word or two may be devoted to the description of the mode of preparation of the vaccine.

The procedure we adopt is as follows:—

We add to a 24 hours' growth of staphylococcus on sloped agar tube about 10 c.c. of sterile physiological salt solution. Churning up our culture with this, and letting it stand in order to allow all the unresolved bacterial masses to subside, we draw off the supernatant fluid by syphon action into a special form of tube and heat to 60° C. for half an hour.

We now place the tube in an incubator and incubate for 24 hours in order to allow of a multiplication of any bacteria which may have survived the heating. We now inoculate a sample of the heated culture upon agar with a view to the detection of any surviving micro-organisms; at the same time, if this has not before been undertaken, we draw off a sample of the suspension and enumerate under the microscope by the procedure described by one of us in the 'Lancet' of July 5, 1902.

After verifying the sterility of the vaccine we now dilute with a sufficiency of physiological salt solution to bring down the number of staphylococci in the cubic centimetre to 2,500,000,000. Finally we add lysol in sufficient quantity to bring the content of the vaccine in this antiseptic to 0·25 per cent.

In connection with boils and sycosis a vaccine made from the *Staphylococcus aureus*; in cases of acne a vaccine made from a mixture of *Staphylococcus albus* and *citreus* is appropriate.

A dose of 0·5 to 1 c.c. of the vaccine made as above is a suitable quantum for a first inoculation. For subsequent inoculations 1 to 2 c.c. of the vaccine may be employed.

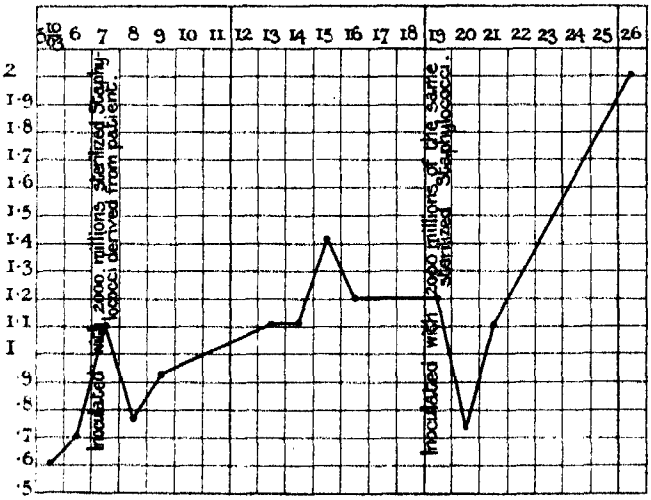
Below are subjoined four of the more instructive of the curves which we have obtained by the periodical examination of the phagocytic power of the blood subsequent to inoculations of staphylococcus vaccines.

Curve 1.—The curve here in question applies to a medical man who had suffered from boils almost continuously for 4 years.

On the date when he presented himself for treatment he had two boils on his neck. It will be seen that the phagocytic ratio recorded for that day was 0·6—the phagocytic power of the normal control blood being throughout taken as unity.

On the next day and the day subsequent phagocytic ratios of 0·7 and 1·1 respectively were recorded. This altogether spontaneous improvement of the phagocytic power went hand in hand with a striking improvement in the condition of the boils.

CURVE 1.



The patient was now inoculated with a quantum of sterilised culture of staphylococcus corresponding to 2,000,000,000 of staphylococci. The culture employed was derived from the patient's boils.

On the day subsequent to inoculation the patient's phagocytic power was found to be reduced. Contemporaneously with the development of this "negative phase," an irritable pimple developed on the neck. We may see in this, for it is a phenomenon which has manifested itself again and again in this connection with our inoculations, an indication that the negative phase is associated with a diminished resisting power to invasion by the staphylococcus.

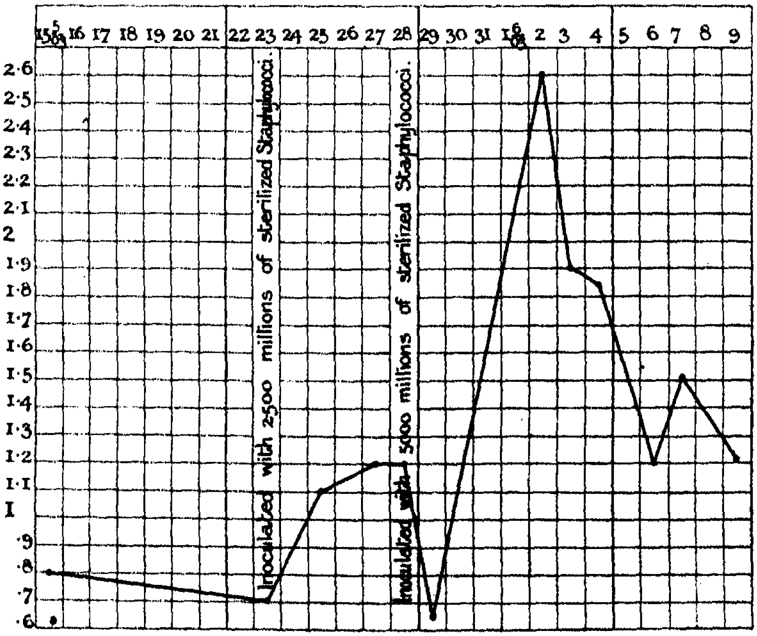
On the second day after the inoculation an improvement in the phagocytic power was recorded. The "positive phase," which is here heralded, reached its acme on the eighth day subsequent to inoculation.

On the twelfth day the patient was re-inoculated with the same quantum of vaccine as was employed on the first occasion. As on the previous occasion, inoculation was followed by a negative, succeeded by a positive phase. For a period of weeks after the inoculation, when the patient passed out of observation, he remained perfectly free from boils.

Curve 2.—This curve has reference to a patient who suffered from aggravated sycosis. A pure cultivation of *Staphylococcus citreus* was obtained from the inflamed hair follicles. He had been treated without appreciable benefit for 17 months by antiseptics.

Reference to the curve will show that the patient's phagocytic power with respect to the staphylococcus was here, as in the last case, less than that of the normal man who served as a control.

CURVE 2.

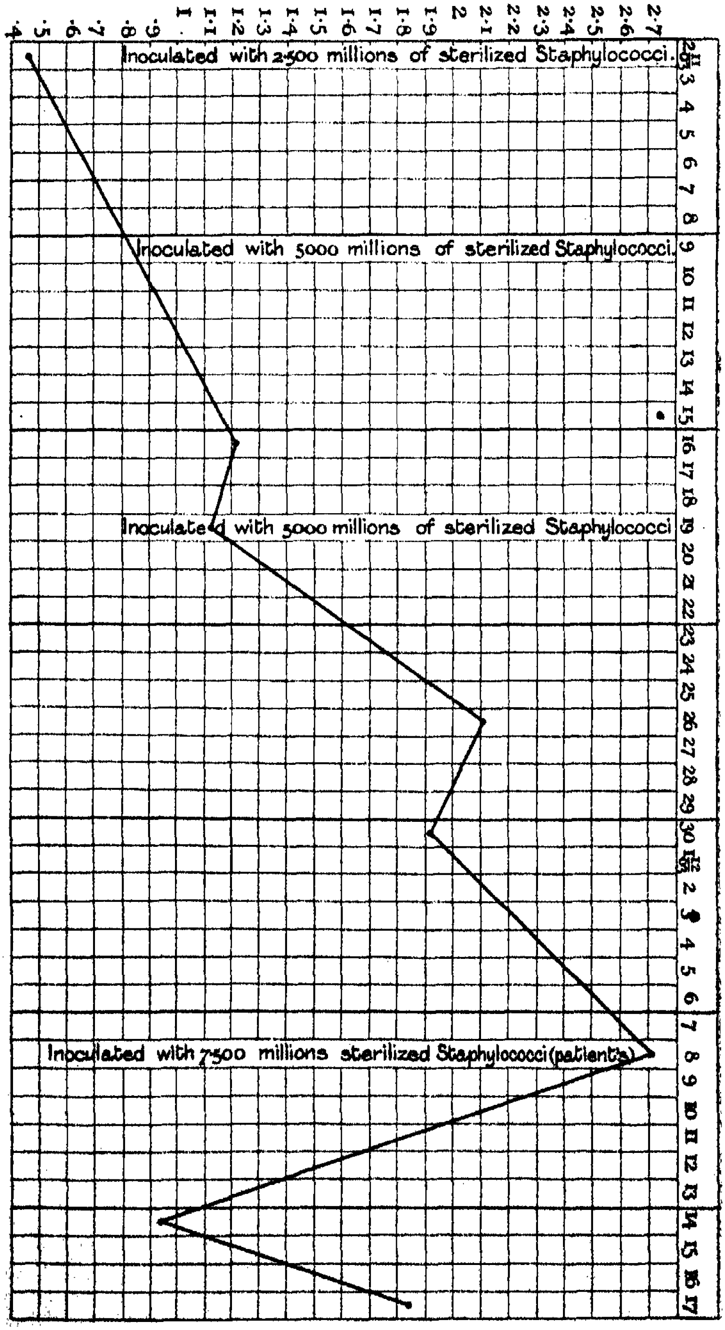


After his phagocytic power had been twice observed, he was inoculated with a quantum of sterilised staphylococcus culture corresponding to 2,500,000,000 of staphylococci. These staphylococci were derived from the culture above referred to.

Subsequent to inoculation we have here upon the curve instead of a rise preceded by a fall, only a rise. The absence of recorded negative phase is in all probability to be referred to the circumstance that 2 days here intervened between the inoculation and the first subsequent blood examination.

On the sixth day subsequent to inoculation the patient was re-inoculated with a double quantum of staphylococcus vaccine. This

CURVE 3.


·4 ·5 ·6 ·7 ·8 ·9 1 1·1 1·2 1·3 1·4 1·5 1·6 1·7 1·8 1·9 2 2·1 2·2 2·3 2·4 2·5 2·6 2·7
Inoculated with 2·500 millions of sterilized Staphylococci.
Inoculated with 5000 millions of sterilized Staphylococci.
Inoculated with 5000 millions of sterilized Staphylococci
Inoculated with 7·500 millions sterilized Staphylococci (patient's)
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17

inoculation was followed in a typical manner by a negative and positive phase. With respect to this last it will be seen that the curve attained its acme on the fifth day, and then declined in the usual manner.

Within a week after the second inoculation practically every trace of sycosis had disappeared. The patient was now lost sight of.

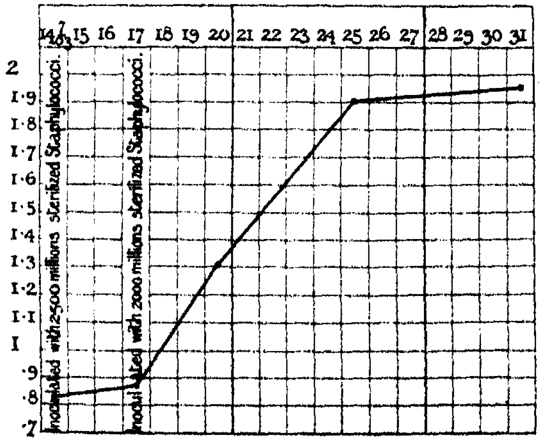
Curve 3.—The curve here in question applies to a labourer who was the subject of aggravated sycosis. He had suffered at intervals from childhood from boils and other chronic staphylococcus infections. A pure cultivation of *Staphylococcus aureus* was obtained from the inflamed hair follicles. He had been treated ineffectually for months by the usual methods.

As will be seen on reference to the chart, the phagocytic power of the blood was here investigated only from week to week instead of at more frequent intervals. As a result the positive phase of the reaction is alone on record in the case of the first three inoculations. In the case of the fourth inoculation—conducted with a larger quantum of the vaccine—the negative phase was still in evidence 6 days after the inoculation.

The patient, who was all but completely cured at the date upon which the curve concludes, afterwards relapsed after free indulgence in alcohol. He is now, as a result of further inoculations, again practically well.

Curve 4.—This curve applies to a healthy man of 24 who, while in training for a boat race, developed a boil on his gluteal region and subsequently a crop of boils on his neck.

CURVE 4.



Reference to the curve will show that his phagocytic index stood at the date of his first inoculation at 0·84.

A quantum of sterilised staphylococcus culture corresponding to 2,500,000,000 of staphylococci was inoculated.

Three days afterwards his phagocytic index stood at 0·88.

A further quantum of 2,000,000,000 staphylococci was inoculated.

On the fifth and again on the eleventh day after inoculation the patient's phagocytic index stood respectively at 1·9 and 1·95.

Improvement in the patient's boils was already apparent at the date of the second inoculation. After this they completely aborted.

The patient afterwards relapsed, but did not come up for further observation.

"On the Action exerted upon the Tubercle Bacillus by Human Blood Fluids, and on the Elaboration of Protective Elements in the Human Organism in Response to Inoculations of a Tubercle Vaccine."

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Communicated by Sir J. BURDON SANDERSON, Bart., F.R.S. Received July 26, 1904.

(From the Pathological Laboratory of St. Mary's Hospital, London, W.)

We propose to consider in this communication (1) the action exerted upon the tubercle bacillus by normal human blood fluids and the tuberculotropic* substances which come here into consideration; (2) the action exerted upon the tubercle bacillus by the blood fluids of those who are the subject of tubercular infection; (3) the distribution of tuberculotropic substances in the infected organism; (4) the question as to whether these protective substances are present in the blood of the infant at birth; and (5) some points in connection with the elaboration in the human organism of tuberculotropic substances in response to inoculations of a tubercle vaccine.

I.—*On the Tuberculotropic Elements of Human Blood and on the Content of the Normal Blood in these Elements.*

Agglutinins.—The technical difficulties created by the circumstance that the tubercle bacillus grows in artificial culture in agglomerated masses stood for a long time in the way of the demonstration of the presence of agglutinins in the serum. These difficulties were for the first time overcome by Arloing, who obtained, by the operation of a process of selection, a strain of tubercle which gives a homogeneous growth when the culture is frequently shaken up. For the homogeneous cultures of Arloing, Koch substituted a homogeneous suspension of bacillary fragments obtained by the trituration of ordinary tubercle cultures. Koch made his suspension with physiological salt solution.

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* The term *tuberculo-tropic* is, in accordance with the scheme of terminology introduced by Ehrlich, employed by us to connote the property of *turning towards* and entering into chemical combination with the tubercle bacillus.

The test fluid thus constituted exhibits—and this point did not escape the observation of Koch—a proneness to spontaneous agglutination. This defect, and it is a defect which may invalidate the results of any test examination, can, as was pointed out by one of us,* be eliminated by employing in lieu of the 0·85-per-cent. NaCl solution, prescribed by Koch, a 0·1-per-cent. NaCl solution.†

We have in the case of the investigations on agglutination which are embodied in this paper in every case employed this 0·1-per-cent. salt solution both for the dilution of the serum and for the suspension of the tubercle powder.

In some of our more recent experiments we have substituted for the test fluid constituted as above a homogeneous suspension of tubercle bacilli obtained by heating an ordinary tubercle culture to 60° C. for an hour, filtering off the bacterial growth, breaking up this last in a mortar with a solution of 0·1-per-cent. NaCl in 0·5-per-cent. carbolic acid, and finally centrifugalising to remove any bacterial masses which have not been resolved into their elements.

In experiments conducted with either the one or the other of these test fluids agglutination effects are obtained with normal human serum. Conducting the experiments in throttled capillary tubes by the method described by one of us,‡ and taking cognisance of the effect by naked-eye inspection, a complete sedimentation is generally obtained in the 2- and 4-fold dilution and incomplete sedimentation in the 8-fold dilution. With some normal bloods complete sedimentation is obtained up to the 16-fold dilution.

Bactericidal Elements.—Our investigations into the question as to the presence of a bactericidal element in human serum are as yet incomplete.

Opsonins.—As already brought out by us in previous papers,§ the phagocytic effect obtained when bacteria are introduced into the blood is dependent upon an action exerted by the blood fluids directly upon the micro-organisms.

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* Wright 'Lancet,' July 25, 1903.

† The principle which suggested the replacement of the stronger by the weaker salt solution finds application, as one of us (S. R. D.) has recently elicited, also in the case of plague cultures. The spontaneous agglutination which has up to the present been a source of difficulty in measuring the agglutination effect exerted by sera upon plague cultures can be completely avoided by employing a 0·1-per-cent. solution of salt in lieu of the broth or physiological salt solution ordinarily employed.

‡ Wright, *loc. cit.*

§ 'Roy. Soc. Proc.,' vols. 72 and 73.

We have investigated this question also in connection with the tubercle bacillus. In doing so a two-fold technical difficulty confronted us :—*first*, a difficulty associated with the circumstance that the tubercle bacillus is available in ordinary cultures only in the form of agglomerated bacterial masses, and *secondly*, a difficulty associated with the circumstance that unaltered tubercle bacilli when they have been obtained in homogeneous suspension are agglutinated by the action of both serum and physiological salt solution.

The first difficulty can be surmounted by breaking up the bacterial masses in a mortar in a 0·1-per-cent. NaCl solution, *i.e.*, in a salt solution diluted up to the point at which it will no longer bring together by its agglutinating action tubercle bacilli which have been mechanically separated.

The second difficulty can be surmounted by heating the tubercle culture to 100° C.

We subjoin here a series of experiments (conducted before the procedure last mentioned was thought out), with living tubercle bacilli suspended in a 0·1-per-cent. NaCl solution. It will be seen that the difference between the phagocytic effect obtained with the unheated and the heated serum respectively is sufficiently pronounced to throw altogether into the background the source of disturbance which is associated with the presence of an agglutinating element in the serum.

PRELIMINARY EXPERIMENTS.

In this series of experiments a homogeneous suspension of living tubercle bacilli was made by rubbing up a small quantity of a tubercle growth (obtained from a glycerine potato culture) in an agate mortar in 1-*in*-1000 *NaCl solution, and then centrifugalising to get rid of the bacterial masses which had not been resolved into their elements.*

Experiment 1.

A.

A. E. W.'s unheated serum....................	2 vols.
S. R. D.'s washed corpuscles....................	2 „
Suspension of living tubercle bacilli	1 vol.

Phagocytic index (average of 67 P.W.B.C.), 5·4.

B.

A. E. W.'s serum heated to 60° C. for 20 mins. ...	2 vols.
S. R. D.'s washed corpuscles....................	2 „
Suspension of living tubercle bacilli	1 vol.

Phagocytic index (average of 80 P.W.B.C.), 0·75.

Experiment 2.

A.

S. R. D.'s unheated serum	2 vols.
S. R. D.'s washed corpuscles	2 ,,
Suspension of living tubercle bacilli	1 vol.

Phagocytic index (average of 16 P.W.B.C.), **17·3.**

B.

S. R. D.'s serum heated to 60° C. for 20 mins.	2 vols.
S. R. D.'s washed corpuscles	2 ,,
Suspension of living tubercle bacilli	1 vol.

Phagocytic index (average of 37 P.W.B.C.), **3·0.**

Experiment 3.

A.

C. J.'s unheated serum	2 vols.
S. R. D.'s washed corpuscles	2 ,,
Suspension of living tubercle bacilli	1 vol.

Phagocytic index (average of 19 P.W.B.C.), **14.**

B.

C. J.'s serum heated to 60° C. for 20 mins.	2 vols.
S. R. D.'s washed corpuscles	2 ,,
Suspension of living tubercle bacilli	1 vol.

Phagocytic index (average of 37 P.W.B.C.), **3·0.**

With cultures which have been exposed to a temperature of 100° C. precisely similar results are obtained, while an advantage is gained in the respect that the count is no longer rendered difficult by the massing together of the bacilli.

All the experiments hereafter subjoined have been carried out with such a culture, *i.e.*, a culture heated to 100°, broken up in 1-in-1000 NaCl solution, and centrifugalised until all unresolved clumps had been carried down.

Our next series of experiments was undertaken with a view to determining whether the increased phagocytic effect obtained with the unheated serum is due to an action exerted by the serum directly upon the tubercle bacilli.

Experiment 1.

A.

S. R. D.'s unheated serum	2 vols.
A. E. W.'s washed corpuscles	2 ,,
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 20 P.W.B.C.), **6·9.**

B.

S. R. D.'s unheated serum	2 vols.
Suspension of heated tubercle bacilli	1 vol.

The above were digested together for 15 mins. at 37° C.; were then heated to 60° C. for 10 mins.; and finally 3 vols. of the mixture were added to

A. E. W.'s washed corpuscles	2 vols.

Phagocytic index (average of 31 P.W.B.C.), **3·5**.

C.

S. R. D.'s unheated serum	2 vols.
Suspension of heated tubercle bacilli	1 vol.

The above were immediately, after mixture, heated to 60° C. for 10 mins., and were then added to

A. E. W.'s washed corpuscles	2 vols.

Phagocytic index (average of 50 P.W.B.C.), **0·16**.

Experiment 2.

A.

A. E. W.'s unheated serum	2 vols.
A. E. W.'s washed corpuscles	2 ,,
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 49 P.W.B.C.), **5·2**.

B.

A. E. W.'s unheated serum	2 vols.
Suspension of heated tubercle bacilli	2 ,,

The above were digested together for 15 mins. at 37° C.; were then heated to 60° C. for 10 mins.; and finally 3 vols. of the mixture were added to

A. E. W.'s washed corpuscles	2 vols.

Phagocytic index (average of 40 P.W.B.C.), **2·6**.

C.

A. E. W.'s unheated serum	2 vols.
Suspension of heated tubercle bacilli	1 vol.

The above were immediately after mixture heated to 60° C. for 10 mins.; and were then added to

A. E. W.'s washed corpuscles	2 vols.

Phagocytic index (average of 50 P.W.B.C.), **0·34**.

Experiment 3.

A.

H. B. S.'s unheated serum	2 vols.
A. E. W.'s washed corpuscles	2 „
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 20 P.W.B.C.) **4·8.**

B.

H. B. S.'s unheated serum	2 vols.
Suspension of heated tubercle bacilli	1 vol.

The above were digested together for 15 mins. at 37° C.; were then heated to 60° C. for 10 mins.; and finally 3 vols. of the mixture were added to

A. E. W.'s washed corpuscles	2 vols.

Phagocytic index (average of 30 P.W.B.C.), **2·6.**

C.

H. B. S.'s unheated serum	2 vols.
Suspension of heated tubercle bacilli	1 vol.

The above were immediately after mixture heated together for 10 mins. to 60° C.; and were then added to

A. E. W.'s washed corpuscles	2 vols.

Phagocytic index (average of 20 P.W.B.C.), **0·4.**

It will be manifest that these experiments testify to an opsonic action exerted by the serum directly upon the tubercle bacilli.

The smaller phagocytic effect recorded in each experiment in B as compared with A is at present without explanation.

The experiment next subjoined indicates that it is the potency of the serum rather than the potency of the white corpuscles which determines the amount of phagocytosis. In this experiment the corpuscles of the tubercular patient's blood, and the corpuscles of the normal blood respectively were employed in A′ and A″ in combination with their native blood fluid. In B′ and B″ a reciprocal exchange of blood fluids was made.

A′.

Patient's washed corpuscles	2 vols.
Patient's serum	2 „
Suspension of heated tubercle bacilli	1 „

Phagocytic index (average of 36 P.W.B.C.), **0·66.**

A″.

A. E. W.'s washed corpuscles	2 vols.
A. E. W.'s serum	2 „
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 32 P.W.B.C.), **3·1.**

B′.

Patient's washed corpuscles	2 vols.
A. E. W.'s serum	2 „
Suspension of living tubercle bacilli	1 vol.

Phagocytic index (average of 31 P.W.B.C.), **2·1.**

B″.

A. E. W.'s washed corpuscles	2 vols.
Patient's serum	2 „
Suspension of living tubercle bacilli	1 vol.

Phagocytic index (average of 30 P.W.B.C.), **1·3.**

It will be seen that the phagocytic effect obtained with the patient's white corpuscles (in A′) was (in B′) increased more than three-fold in consequence of the replacement of their native serum by that of the control blood. The phagocytic effect obtained with the white corpuscles of the control blood (in A″) was (in B″) diminished in an almost corresponding degree (approximately two and a half times), by the replacement of their native serum by that of the patient.

These results are, it may be pointed out, in conformity with those recorded in our previous paper* in connection with the phagocytosis of the staphylococcus pyogenes.

II.—*Action exerted upon the Tubercle Bacillus by the Blood-fluids of those who are the subject of Tubercular Infection.*

The blood fluids of the subjects of a particular bacterial infection may be expected to differ with respect to their content in bacteriotropic substances from the blood fluids of normal persons. An increased content in these elements may be expected in the case where there has been active response on the part of the machinery of immunisation to the stimulus of infection; diminished content (*a*) where that machinery is becoming exhausted, and (*b*) where infection is dependent upon a native, or at any rate, antecedent deficiency in protective substances.

Agglutinating effect.—We have in no instance found the agglutinating power of the blood of tubercular patients higher than that of certain normal bloods. Sometimes we have found it notably decreased. In three cases we have found it altogether absent. On the average we find that it does not differ sensibly from that of the normal blood.

It would seem to follow—and this conclusion is in conformity with that arrived at by others—that no indication as to the presence or absence of tubercular infection can be drawn from the measurement of the agglutinating power, unless perhaps in the case where that reaction is found to be quite absent.

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* 'Roy. Soc. Proc.,' vol. 73, pp. 129 and 130.

Opsonic effect.—The measurement of the opsonic power of the blood fluids discloses very definite differences. We have not in any of the sub-joined patients recorded at the outset an opsonic power equal to that of our own bloods. On the contrary there has been in each such case a definite defect of opsonic power. The results of our observations on this point are embodied in the table below.

Table I.—Showing the Opsonic Power of the Blood Fluids in a Series of Tubercular Patients.

The procedure adopted was to mix together in each case the patient's serum with a suspension of heated tubercle bacilli and with washed corpuscles derived from a normal person. In each case the opsonic power of the normal serum employed as a control (derived in practically every case from A. E. W. or S. R. D.) was taken as unity.

Serial number of the observation.	Form of the tubercular infection.	Opsonic index.
Case 1	Tubercular peritonitis	0·67
,, 2	Laryngeal phthisis	0·6
,, 3	Psoas abscess	0·4
,, 4*	Tubercular sycosis	0·4
,, 5	Nasal and pharyngeal lupus	0·56
,, 6	Tubercular cystitis	0·8
,, 7	,, ,,	0·6
,, 8	Generalised lupus	0·5
,, 9	Lupus of hand	0·9
,, 10	Tubercular prostatitis	0·8
,, 11	,, glands	0·85
,, 12	,, abscess of thigh	0·64
,, 13†	Lichen scrophulosorum	0·56
,, 14	Pulmonary phthisis	0·75
,, 15	,, ,,	0·69
,, 16‡	Tubercular infection of ovary and peritonitis	0·65
,, 17	,, abscesses of arm and chest wall	0·56

As indicated above, a diminished content in bacteriotropic substances such as we have here on record may be ascribed either to the exhaustion of the protective elements under the influence of the bacterial invasion; or, alternatively, *to an antecedent deficiency in these elements.*

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* It is interesting to note in connection with this case that the definite diagnosis of tubercular infection, which was based upon the histological structure of a piece of excised tissue, was anticipated in view of the inductions obtained from the phagocytic test recorded above.

The alternative diagnosis of staphylococcus infection was excluded by the fact that the patient was found to possess a normal opsonic index with respect to the staphylococcus.

† The patient gave a typical local and general reaction when inoculated for diagnostic purposes with a test dose of Koch's old tuberculin.

‡ The diagnosis was based upon a histological examination of the extirpated ovary.

The following considerations appear to us here to plead in favour of interpreting the low opsonic power of the tubercular patients here in question as the occasion and not the consequence of infection.

(*a*) Very low phagocytic indices have been obtained where constitutional symptoms were absent or insignificant. The cases denoted by the serial numbers 3, 4, 5, and 8 are instances in point.

(*b*) We have in practically every case found it possible to increase by an inoculation of a tubercle vaccine, the opsonic power of a patient's blood fluids.

III.—*Distribution of Tuberculotropic Substances in the Infected Organism.*

We have made the subjoined observations on this question. It will be seen that they are in consonance with the observations (see pp. 151—153) we have made in connection with the distribution of the staphylococcic opsonins in the infected organism, and with the induction that the bacteriotropic pressure is always reduced in the actual foci of infection.

Observation 1.

The patient was a child æt. 2 years, affected with tubercular necrosis of the sternum, and with a tubercular abscess in the thigh.

A.

Serum obtained from blood drawn from finger	1 vol.
Physiological salt solution	1 ,,
S. R. D.'s washed corpuscles	2 vols.
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 20 P.W.B.C.), 3·9.

B.

Supernatant fluid of pus withdrawn from abscess	1 vol.
Physiological salt solution	1 ,,
S. R. D.'s washed corpuscles	2 vols.
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 20 P.W.B.C.), 1·1.

Observation 2.

The patient was a young man suffering from a psoas abscess due to tubercular infection.

A.

Serum obtained from blood withdrawn from finger	1 vol.
Physiological salt solution	1 ,,
A. E. W.'s washed corpuscles	2 vols.
Suspension of heated tubercle bacilli	2 ,,

Phagocytic index (average of 40 P.W.B.C.), 0·6.

B.

Supernatant fluid of pus derived from sinus	1 vol.
Physiological salt solution	1 „
A. E. W.'s washed corpuscles	2 vols.
Suspension of heated tubercle bacilli	2 „

Phagocytic index (40 P.W.B.C. searched), **0.**

With a view to ascertaining whether the tissue lymph might not normally be poorer in opsonic substances than the serum, the following experiment was made :—

A.

Serum of blood withdrawn from A. E. W.'s finger	2 vols.
A. E. W.'s washed corpuscles	2 „
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 50 P.W.B.C.), **0·92.**

B.

Fluid from blister raised by friction upon A. E. W.'s finger	2 vols.
A. E. W.'s washed corpuscles	2 „
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 50 P.W.B.C.), **0·86.**

Observation 3.

The patient was a young man operated upon for ascites dependent upon extensive tubercular infection of the peritoneum.

A.

Serum obtained from blood withdrawn from finger	1 vol.
B. H. S.'s washed corpuscles	1 „
Suspension of heated tubercle bacilli	1 „

Phagocytic index (average of 21 P.W.B.C.), **25·4.**

B.

Fluid withdrawn from peritoneum	1 vol.
B. H. S.'s washed corpuscles	1 „
Suspension of heated tubercle bacilli	1 „

Phagocytic index (average of 34 P.W.B.C.), **4·6.**

It is interesting to bring into relation with the data of this last observation (*a*) the fact that the opsonic index of this patient's serum stood to the opsonic index of the control serum employed (A. E. W.'s) as 1·5 : 1 ; (*b*) the fact that the prognosis, so far as the restriction of the infection to the existing focus of disease, is comparatively favourable in cases of tubercular peritonitis ; and (*c*) the fact that a retrogression of the infection often follows in these cases upon the evacuation of the peritoneal fluid.

The *first* and *second* of these facts suggest that a reaction of immunisation may be set up by the absorption of vaccinating elements from the infected peritoneum. The *third* fact, and the same applies (*vide* Case 1, p. 152, of the foregoing paper) also in connection with the evacuation of abscesses may, perhaps, find its explanation in the data given above. It would be reasonable to expect that the flow of new and active lymph, which would follow upon the evacuation of the stagnant and exhausted lymph, would operate in the direction of checking the growth of invading micro-organisms.

IV.—*Question as to whether the Protective Substances which come into consideration in connection with Tubercle are present in the Blood of the Infant at Birth.*

In view of the asserted superior susceptibility of infants to tubercular infection, it appeared to us to be of interest to measure the respective opsonic power of mother and infant. We employed for this purpose blood taken from the umbilical cord and blood taken from the mother's finger immediately after completion of labour. Our observations are subjoined.

Observation 1.

A.

Serum from mother No. 1	2 vols.
A. E. W.'s washed corpuscles	2 „
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 45 P.W.B.C.), 1·6.

B.

Serum of infant No. 1	2 vols.
A. E. W.'s washed corpuscles	2 „
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 50 P.W.B.C.), 1·38.

Observation 2.

A.

Serum of mother No. 2	2 vols.
A. E. W.'s washed corpuscles	2 „
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 50 P.W.B.C.), 0·4.

B.

Serum of infant No. 2	2 vols.
A. E. W.'s washed corpuscles	2 „
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 100 P.W.B.C.), 0·87.

Observation 3.

A.

Serum of mother No. 3	2 vols.
J. F.'s washed corpuscles	2 ,,
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 40 P.W.B.C.), **3·55.**

B.

Serum of child No. 3	2 vols.
J. F.'s washed corpuscles	2 ,,
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 40 P.W.B.C.), **1·85.**

Observation 4.

A.

Serum of mother No. 4	2 vols.
A. E. W.'s washed corpuscles	2 ,,
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 31 P.W.B.C.), **17·9.**

B.

Serum of infant No. 4	2 vols.
A. E. W.'s washed corpuscles	2 ,,
Suspension of heated tubercle bacilli	1 vol.

Phagocytic index (average of 30 P.W.B.C.), **10.**

Observation 5.

A.

Serum of mother No. 4 agglutinates a suspension of fragments of tubercle bacilli completely in dilutions of 1 in 2, 4, 8, and 16; incompletely in a dilution of 1 in 32.

B.

Serum of infant No. 4 agglutinates the same suspension completely in dilutions of 1 in 2 and 1 in 4; incompletely dilutions of 1 in 8 and 1 in 16.

V.—*On some points in connection with the Elaboration by the Human Organism of Tuberculotropic Elements in response to Inoculations of a Tubercle Vaccine.*

We propose to set down here in briefest outline the more important of the facts which have emerged in the course of a study of the blood changes elicited by inoculations of a tubercle vaccine undertaken for therapeutic purposes.

Nature of the Tubercle Vaccine employed.—A tubercle vaccine may be defined, with respect to its derivation and its effect upon the organism, as any derivative of the protoplasm of the tubercle bacillus, which is capable of inducing an elaboration of tuberculotropic substances in the organism.

We may include under this definition:—

(1) Such a vaccine as would be arrived at by (*a*) sterilising a tubercle culture at 60° C.; (*b*) breaking up the culture in a mortar in 0·1-per-cent. salt solution; (*c*) centrifugalising to remove any residual bacterial masses; (*d*) resterilising at 60° C.; and (*e*) standardising by enumeration, or by centrifugalisation in graduated tubes in a sufficiently concentrated salt solution.

(2) The preparation, which is sold, as a therapeutic agent, under the name of Koch's new tuberculin or T.R. tuberculin.

This preparation consists, as is well known, of a fine suspension of triturated tubercle bacilli. The trituration to which the tubercle culture is subjected is employed with the two-fold object of sterilising the vaccine by a process of comminution, and of obtaining the fine suspension which is desired.

It is doubtful whether the first of those ends can be efficiently secured by any process of trituration. The homogeneous suspension which is desired can, as was shown above, be obtained by means other than the comminution of the bacilli by machinery.

(3) The preparation, which is now sold, chiefly for diagnostic uses, under the name of Koch's old tuberculin.*

This preparation consists, as is well known, of the inspissated filtrate of a tubercle culture which has been grown for a period of weeks upon glycerinated broth, and which has afterwards been sterilised at 100° C.

Pending the working out of a vaccine upon the lines indicated in (1), the T.R. tuberculin has been the vaccinating material employed.

In our earlier experiments this preparation was simply diluted with sterilised salt solution.

In our later experiments we have—after satisfying ourselves that the vaccinal properties of Koch's preparation are unaffected by the adoption of such precautions—in every case heated the T.R. tuberculin to 60° C. for 1 hour, and have made our dilutions with a sterilised salt solution which had received an addition of 0·25 per cent. lysol.

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* The proposition that the old tuberculin may appropriately be denoted a vaccine derives its justification, first, from the consideration that the prolonged cultivation and the prolonged digestion of the culture which is involved in the process of manufacture must be associated with autolysis, and secondly, from the observations made in connection with Case 13 of Table I and the last patient in Table III.

In the former case, the opsonic index of the patient's blood stood at 0·56 immediately before the inoculation of 1 millegramme old tuberculin. It stood at 0·55 18 hours afterwards in the height of the febrile reaction, and at 1·01 3 days later.

In the latter case, the opsonic index of the blood stood at 0·67 immediately before the inoculation of 1 millegramme of the old tuberculin. It stood next day at 0·4, and 8 days later at 0·76.

Principle upon which the Patients were Selected and General Procedure Followed in Connexion with the Inoculations.

We have in our selection of cases been guided by the desire to deal at first only with the most aggravated and seemingly intractable cases of localised tubercular infection, and only with cases which would furnish unambiguous objective evidence of any progress or regress of the infection.

The general procedure followed was to begin in each case after the measurement of the content of the patient's blood in tuberculotropic substances, with very small doses (generally 1/500th milligramme) of the vaccinating material, and to reinoculate at intervals of 10 days, retesting the blood on each occasion, and in the case of each patient expressing the results in the form of a curve.

In our earlier experiments, before we had elaborated the procedure for measuring the opsonic power of the blood, we were necessarily restricted to a measurement of the agglutinating power.

Data Furnished by the Measurement of the Agglutinating Power in the Case of Patients Undergoing Anti-Tubercle Inoculation.

The method of investigation here in question—and we would note that it had before us been employed by Koch in connection with inoculations of his T.R. tuberculin—furnishes, it seems to us, indications which have a certain value.

An increase in the agglutinating power of the blood is generally, as in the cases tabulated below, obtained in the course of a successful immunisation.

It is, however, to be noted that the rise in the agglutination curve may occur long subsequent to the achievement of very marked clinical improvement, and further that such clinical improvement may be obtained quite apart from any sensible increase in the agglutinating power of the blood.

Table II.—Showing the Agglutinating Power of the Blood in the case of a Series of Patients, before Inoculation, and after a Series of Inoculations of Tubercle Vaccine.

Patient's initials.	Highest dilution of serum in which complete agglutination was obtained, and date of observation (in brackets).	Highest dilution of serum in which complete agglutination was obtained after the inoculations particularised in the next column, and date of observation (in brackets).	Doses of T.R. tuberculin, and dates of inoculations (in brackets).
			mgrm.*
A. R.	3 (2.12.03)	32 (23.3.04)	0·0025 (2.12.03) 0·01 (17.12.03) 0·01 (4.1.04) 0·01 (14.1.04) 0·0075 (21 1.04) 0·0075 (1.2.04) 0·015 (15.2.04) 0·02 (1.3.04) 0·04 (11.3.04)
J. A.	0 (6.4.03)	64 (21.4.03)	0·002 (6.4.03) 0·01 (8.4.03) 0·02 (15.4.03)
N. T.	4 (6.1.04)	64 (23.3.04)	0·003 (20.1.04) 0·005 (2.2.04) 0·01 (23.2.04) 0·015 (2.3.04) 0·02 (12.3.04)
N. W.	8 (10.12.03)	32 (20.3.04)	0·01 (17.12.03) 0·0075 (4.1.04) 0·0075 (19.1.04) 0·01 (28.1.04) 0·01 (10.2.04) 0·015 (19.2.04) 0·02 (3.3.04) 0·02 (14.3.04)
E. J.	4 (27.1.04)	32 (16.3.04)	0·003 (27.12.03) 0·0066 (11.1.04) 0·01 (28.1.00) 0·015 (1.3.04)
E. S.	2 (17.4.03)	64 (30.4.03)	0·005 (21.4.03) 0·01 (24.4.03)
M. O.	0 (15.12.03)	24 (17.2.04)	0·004 (28.12.03) 0·008 (5.1.04) 0·016 (21.1.04)

* The weights here in question refer in each case to the weight of tubercle powder stated to be contained in the quantum of T.R. tuberculin administered.

In addition to furnishing indications of successful advance in the direction of immunisation, the measurement of the agglutinating power of the patient's blood may afford also indications of regress in the direction of increased susceptibility resulting from an overtaxing of the machinery of immunisation.

In exemplification of this we may quote three passages from the history of a patient (E. S. Tables II and III) with tubercular infection of the kidney and bladder, whose agglutination curve was followed for nearly 18 months.

The patient in question, who had in association with the inoculations set forth in Table II put on 5 lbs. in weight, received on April 30, the date on which the record in Table II closes, 0·025 milligramme on May 5, 0·05 milligramme, and on May 13, 0·2 milligramme of T.R. tuberculin.

In association with the first two of these inoculations, the agglutination curve sank away rapidly from 64 to 8, the patient losing at the same time 3½ lbs. in weight, and suffering from considerable constitutional disturbance.

In association with the third of these inoculations the agglutinins disappeared entirely from the blood.

On a later occasion in the beginning of November, 1903; when the general condition of the patient had very markedly improved and when her body weight had increased by 23 lbs., a similar negative phase effect accompanied by constitutional disturbance was obtained in association with the inoculation of three 1 milligramme doses of the T.R. tuberculin on November 2, 6, and 11 respectively. Here the complete agglutination, which was on the first of these dates obtained in a 32-fold dilution of the serum, was obtained after the inoculations only in an 8-fold dilution.

Again, in the beginning of December when another attempt was made to press the inoculations, the agglutination curve, which had risen again to 32 after the inoculations referred to in the preceding paragraph, declined in consequence of two 1 milligramme inoculations, first to 8 and then to 2, and the patient's symptoms were aggravated.

A similar decline of the agglutination curve has come under observation also in other cases in association with the premature increase of the dose of vaccine, and with the shortening of the interval between successive inoculations.

Data furnished by the measurement of the Opsonic Power of the Blood in the case of Patients undergoing Anti-tubercle Inoculations.

Much more valuable than the indications which can be gleaned from the measurement of the agglutinating power of the blood are the indications furnished by a measurement of the opsonic power of the patient's blood. While the measurement of the agglutinating power of the blood may fail to furnish indications of an abnormally low resisting power on the part of the untreated patient; and while it may yield only tardy information of the alterations effected in the blood fluids by inoculation; and while it may sometimes altogether fail to distinguish between the patient's condition before and after successful immunisation; the measurement of the opsonic power satisfies it would seem all these desiderata.

We have already seen in Table I that it distinguishes* between the tubercular subject and the person with normal resistance. And we shall see in the table below that it furnishes prompt and clear indication of the negative phase which supervenes upon inoculation, and again of the positive phase which succeeds the negative phase wherever the organism possesses the necessary power of response. Furthermore the measurement of the opsonic power of the blood distinguishes clearly between the untreated tubercular patient and the patient who has made progress in the direction of immunisation. This will appear clearly on comparing, in Table III below, the opsonic indices achieved after inoculation with those set forth in Table I.

In conclusion we may note, that while we are jointly responsible for the observations set forth in Sections 1, 3, and 4 of this paper, the work which is embodied in Sections 2 and 5 has been separately undertaken by one of us.

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* It will not, however, invariably do so.

Table III.—Shows the Changes induced in the Opsonic Power of the Blood Fluids by the Inoculation of Tubercle Vaccine, and furnishes Illustration of the Fact that the Cumulative Increase of the Protective Elements which is desired can be achieved only by the Proper Regulation and Interspacing of the Successive Doses of Vaccine.

Initials.	Brief history of case.	Dates and particulars of inoculations undertaken since March, 1904.	mgrm.*	Opsonic index (opsonic power of the normal blood —A. E. W.'s— used as a control was taken as = 1).
E. J.	Patient, a man of 30, developed tubercular glands on the left side of neck and a tubercular abscess on the point of the shoulder in the autumn of 1902. He was admitted to hospital and was operated upon for the first time in January, 1903. The wounds becoming invaded with tubercle, and refusing to heal, while the area of infection gradually extended, six further (scraping, extirpating, and skin-grafting) operations were undertaken during the course of the year. In December, 1903, when patient came up for treatment by inoculation, the whole area from the point of the shoulder to the ear had been converted into an ulcerated surface, there was a deep crater undermining the angle of the jaw and the ear, the left side of the face was distorted with swelling, and the axilla was occupied by a gland as large as a pigeon's egg. The patient was very anæmic and emaciated. Steady improvement has been made under the inoculation treatment, the swelling of the face has almost entirely dispersed, the cavity under the jaw has healed up from the bottom, the gland in the axilla can no longer be felt, the ulcerated wound surfaces have almost completely closed, and the patient has the constitutional aspect of a healthy man.	28.3.04	0·04	
		18.4.04	0·1	0·73
		25.4.04	0·1	
		10.5.04	0·1	
		7.6.04	0·1	1·6
		27.6.04	nil	1·45
		15.7.04	0·02	
		19.7.04	nil	1·15

Note.—During the period 7.6.04—15.7.04 the inoculations of tubercle vaccine were suspended while the patient was being immunised against the staphylococcus pyogenes, which, by its presence on wound, appeared to be preventing the process of healing.

E. S. ……	Patient came into hospital in December, 1902, with the characteristic symptoms of an infection of the urinary tract. Tubercle bacilli were constantly present in phenomenal numbers in the urine, and a tubercular ulcer of the bladder was detected. Patient had been losing flesh and suffered from night sweats and from constant pain and frequency. Treatment by inoculation was begun on 21.4.03 and has been continued up to date, inoculations and examinations of the blood and urine being undertaken on an average once in 10 days. Under the treatment the tubercle bacilli in the urine have gradually diminished, and since the beginning of May they have been completely absent. The patient has increased 36 lbs. in weight and is now to all intents and purposes well, except for an infection of the urinary tract by the bacillus coli and pneumococcus, which is being dealt with by the inoculation of the appropriate vaccines.	25.3.04	0·5	
		8.4.04	0·5	0·93
		18.4.04	0·5	0·4
		27.4.04	nil	0·42
		9.5.04	0·5	0·77
		1.6.04	0·5	0·4
		15.6.04	nil	1·3
		6.7.04	nil	2·2

Note.—The results of the blood examinations bring out that the inoculations were here conducted with excessive doses or perhaps at too short intervals. It will be seen that the opsonic power of the patient's blood declined in consequence of the inoculation undertaken on 8.4.04 from 0·93 on that date to 0·4 on 18.4.04. On the date last mentioned another 0·5 milligramme was inoculated—and it may be noted in this connection that here as elsewhere it was often necessary to inoculate before the result of the blood examination was known. On 27.4.04 recovery was still incomplete, the patient being obviously poorly and the inoculation was postponed. When next examined 12 days later the opsonic power of the blood was found to have risen to 0·77. A further dose of 0·5 milligramme was then inoculated, with the result that the opsonic power was reduced again to 0·4 on 1.6.04. On this day the patient again received a dose of 0·5 milligramme, the effect of this became manifest 14 days after in the rise of the opsonic power to 1·3 and 36 days after in the rise of opsonic power to 2·2.

N. W. ……	Patient, a woman 31 years of age, developed a tubercular infection of the glands of the neck at the age of 14. When the abscesses which formed in association with these were opened the overlying skin became invaded, the infection spread to other glands, and tubercular disease developed in the little finger of the right hand. The two terminal joints of this finger were removed when the patient was 16. When the patient was 19 she was treated with Koch's old tuberculin, receiving three to four inoculations a day (150 inoculations in all). As a result of these inoculations the patches of lupus on hand, neck and face became inflamed, a piece of bone sloughed out of the arm and the patient lost weight and became seriously ill. She remained in hospital in all 13 weeks.	18.4.04	0·04	0·16
		3.5.04	0·05	0·6
		16.5.04	0·05	—
		1.6.04	0·05	0·78
		10.6.04	nil	—
		19.6.04	0·04	—
		6.7.04	0·04	1·85
		22.7.04		1·7

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* The weights here in question refer in each case to the weight of tubercle powder stated to be contained in the quantum of T.R. tuberculin administered.

Table III—*continue*.

Initials.	Brief history of case.	Dates and particulars of inoculations undertaken since March, 1904.		Opsonic index (opsonic power of the normal blood—A. E. W.'s—used as a control was taken as = 1).
	Four years later energetic local treatment was adopted and scraping operations were undertaken upon the glands in the neck. In 1900 the Finsen light treatment was adopted, and was persevered in for 18 months. This effected an improvement in the condition of the face and neck, but the disease continued to extend in the deeper structures, and in particular in the bones of the left arm. Finally it became necessary to amputate this limb. The disease now broke out in the stump, on the point of the shoulder and in the chest wall, while it persisted all over both sides of the face and neck. After Röntgen rays had been tried unavailingly, recourse was had to inoculations of tubercle vaccine, the *treatment being begun on December 10, 1903.* After 6 months treatment the discharge from the stump and chest wall has *practically ceased, the patch on the point of the shoulder has healed up,* the face appears to be in a better condition, and the patient's general health, which was *previously very unsatisfactory,* has improved in a remarkable manner. Her body weight has steadily gone up and has now reached 141¼ lbs., *as much as 5 lbs. having* on one occasion been gained in the *interval between two successive inoculations.*		mgrm.	
A. R.	Patient, when referred for treatment by antitubercular inoculations in December, 1903, was found to be an emaciated, anæmic, physically and mentally undeveloped child of 19 affected by lupus of the nose, throat, angle of jaw, and feet and hands. The last were a mass of ulceration, the bones of the hand being involved in many places.	22.3.04	0·02	
		7.4.04	0·05	1·1
		18.4.04	0·1	0·25
		23.4.04	nil	—
		5.5.04	0·05	0·61

	After 6 months' treatment the patches of lupus on the nose and throat have almost dried up and the condition of the hands and feet is much amended.	6.5.04	nil	0·85
		16.5.04	0·1	—
		7.6.04	0·1	1·2
		4.7.04	0·04	0·95
		19.7.04		1·3
		22.7.04	0·04	2·9

Note.—The obviously excessive dose of 0·1 milligramme was administered on 18.4.04 before it had been elicited by blood examination that the patient had not yet responded to the dose of 0·05 milligramme administered on 7.4.04. *As a result—it may be assumed—of this* cumulation of doses considerable constitutional disturbance was experienced. In view of this and of the development of a phlyctenule on the eye (a phenomenon which had once before been noticed in connection with the development of a negative phase) the inoculation fixed for the 28.4.04 was postponed and on the next occasion a smaller dose was administered.

A. A......	Patient, a young man, had been in bed for 12 months with a psoas abscess which discharged continuously and showed no signs of improvement. Treatment by inoculation was begun on April 8th. The patient is reported to have made rapid progress towards recovery immediately after the adoption of the treatment.	8.4.04	0·002	0·4
		20.4.04	0·002	
		3.5.04		0·5
		10.5.04	0·004	
		31.5.04	0·01	
		2.6.04		0·8
		16.6.04		1·1
M. O......	Patient, a young married woman, developed a double psoas abscess which was opened up before and behind, in January, 1903. The discharge from the wound continued till December without any sign of improvement, the temperature reaching 101° F. practically every night. The treatment by inoculations of tubercle vaccine was begun in the middle of December, 1903, and has been continued since that date. The temperature became normal 10 days after the first inoculation, the wounds are practically healed and the patient is able to go out for drives. Her body weight has increased by 16 lbs.	Record of the inoculations which were carried out by the surgeon in charge of the case is not to hand.		
		10.6.04	0·1	
		19.6.04		1·95
S. T......	Patient, a man of 35, is the subject of phthisis associated with tubercular disease of the larynx.	2.6.04	0·002	0·6
		8.6.04		1·15
		9.6.04	0·004	
		21.6.04		0·98
		22.6.04	0·008	
		12.7.04	0·008	0·84
		25.7.04		1·36

Table III—*continued.*

Initials.	Brief history of case.	Dates and particulars of inoculations undertaken since March, 1904.		Opsonic index (opsonic power of the normal blood—A. E. W.'s—used as a control was taken as = 1).
			mgrm.	
S. N.	Patient, a woman æt. 34, developed at age of 14 a tubercular abscess in left shoulder, at age of 16, a similar affection of the right leg behind knee, and at 17, lupus of the hand and foot. The little finger of the right hand was amputated in 1887, the third finger of the same hand in 1903, and three toes in April, 1904. In each case the tubercular infection has recurred in the site of the wound.	13.6.04	0·004	0·9
		21.6.04	0·01	
		27.6.04	0·005	0·7
		5.6.04		0·65
		14.7.04		1·05
		15.7.04	0·008	
		21.7.04		0·73
S. B.	Patient, a man of 22, has been the subject of lupus for the last 15 years. He has been treated by all the ordinary methods, including the application of Röntgen rays. Practically the whole of his face and neck are affected. He has also large patches on the scalp, trunk, and elbow of the right arm.	7.7.04	0·002	0·5
		11.7.04		0·44
		15.7.04	0·004	
		18.7.04		1·3
P. C.	Patient, a woman of 55, has for a long period of years been the subject of lupus of nose. The affection has now spread to her pharynx and larynx.	5.7.04	0·002	0·56
		12.7.04	0·004	0·48
		19.7.04		1·0
J. S.	Patient, a man æt. 35, has suffered for two years from an inflammatory tumefaction of the subcutaneous tissues in the region of the angle of the jaw and anterior portion of the throat. The patient has been treated by scraping and the application of antiseptics.	4.7.04	1·0*	0·67
		5.7.04		0·4
		13.7.04	0·004†	0·76
		21.7.04		1·06

* Old tuberculin.

† New tuberculin.

"On the Density of Nitrous Oxide." By LORD RAYLEIGH, O.M. F.R.S.

Received September 1, 1904.

In the 'Proceedings,' vol. 72, p. 204, 1897,* I have given particulars of weighings of nitrous oxide purified by two distinct methods. In the first procedure, solution in water was employed as a means of separating less soluble impurities, and the result was 3·6356 grammes. In the second method a process of fractional distillation was employed. Gas drawn from the liquid so prepared gave 3·6362. These numbers may be taken to represent the corrected weight of the gas which fills the globe at 0° C. and at the pressure of the gauge (at 15°), and they correspond to 2·6276 for oxygen.

Inasmuch as nitrous oxide is heavier than the impurities likely to be contained in it, the second number was the more probable. But as I thought that the first method should also have given a good result, I contented myself with the mean of the two methods, viz., 3·6359, from which I calculated that referred to air (free from H_2O and CO_2) as unity, the density of nitrous oxide was 1·52951.

The corresponding density found by M. Leduc is 1·5301, appreciably higher than mine; and M. Leduc argues that the gas weighed by me must still have contained one or two thousandths of nitrogen.† According to him the weight of the gas contained in my globe should be 3·6374, or 1·5 milligrammes above the mean of the two methods.

Wishing, if possible, to resolve the question thus raised, I have lately resumed these researches, purifying the nitrous oxide with the aid of liquid air kindly placed at my disposal by Sir J. Dewar, but I have not succeeded in raising the weight of my gas by more than a fraction of the discrepancy (1·5 milligramme). I have experimented with gas carefully prepared in the laboratory from nitrate of ammonia, but as most of the work related to material specially supplied in an iron bottle I will limit myself to it.

There are two ways in which the gas may be drawn from the supply. When the valve is upwards, the supply comes from the vapourous portion within the bottle, but when the valve is downwards, from the liquid portion. The latter is the more free from relatively volatile impurities, and accordingly gives the higher weight, and the difference between the two affords an indication of the amount of impurity present. After treatment with caustic alkali and sulphuric acid, the gas is conducted through a tap, which is closed when it is desired to make a vacuum over the frozen mass, and thence over phosphoric anhydride to the globe. For the details of apparatus, etc., reference must be made to former papers. The condensing chamber, which can be immersed in liquid air, is in the form of a vertical tube, 2½ cm. in diameter and 22 cm. long, closed below and above connected laterally to the main channel.

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* Or 'Scientific Papers,' vol. 4, p. 350.

† 'Recherches sur les Gaz,' Paris, 1898.

The first experiment on July 13 was upon gas from the top of the bottle as supplied, and without treatment by liquid air, with the view of finding out the worst. The weight was 3·6015, about 35 milligrammes too light. The stock of material was then purified, much as in 1896. For this purpose the bottle was cooled in ice and salt* and allowed during about one hour to blow off half its contents, being subjected to violent shaking at frequent intervals. Subsequently three weighings were carried out with gas drawn from the bottom, but without treatment by liquid air. The results stand:—

July 18	3·6368
July 20	3·6360
July 25	3·6362
Mean	3·63633

Next followed experiments in which gas, still drawn from the bottom of the bottle, was further purified by condensation with liquid air. The gas, arriving in a regular stream, was solidified in the condensing chamber. When it was judged that a sufficiency had been collected, the tap behind was turned and a *high* vacuum established over the solid mass with the aid of the Töpler pump. The pump would then be cut off and the gas allowed to evaporate and accumulate in the globe. A reapplication of liquid air caused the gas to desert the globe for the condensing chamber, until in a surprisingly short time a vacuum was re-established. Little or nothing could now be drawn off by the pump, and it was thought that a distinct difference could be perceived between the first and second operations, indicating that in the first condensation a little impurity remained gaseous. If desired, the condensation could be repeated a third time. On one occasion (August 7) the condensed gas was allowed to *liquefy*, for which purpose the pressure must rise to not far short of atmospheric, and to blow off part of its contents:—

August 1	3·6363
August 3	3·6367
August 7	3·6366
Mean	3·63653

The treatment with liquid air raised the weight by only 0·2 milligramme, but the improvement is probably real. That the stock in the bottle still contained appreciable impurity is indicated by a weighing on August 13, in which without liquid air the gas was drawn from the *top* of the bottle. There appeared

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* The lower the temperature below the critical point, the more effective is this procedure likely to be.

August 13 .... 3·6354,

about 1 milligramme short of the proper weight.

It will be seen that the result without liquid air is almost identical with that found by the same method in 1896, and that the further purification by means of liquid air raises the weight only to 3·6365. I find it difficult to believe that so purified the gas still contains appreciable quantities of nitrogen.

The corresponding weight of air being 2·3772,[*] we find that, referred to air as unity, the density of nitrous oxide is

$$\frac{3·6365}{2·3772} = 1·5297.$$

Again, if oxygen be taken as 16, the density of nitrous oxide will be

$$\frac{3·6365 \times 16}{2·6276} = 22·143.$$

The excess above 22 is doubtless principally due to the departure of nitrous oxide from Boyle's law between atmospheric pressure and a condition of great rarefaction. I hope shortly to be in a position to apply the correction which will allow us to infer what is the ratio of molecular weights according to Avogadro's rule.

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[*] 'Roy. Soc. Proc.,' vol. 53, p. 134, 1893; 'Scientific Papers,' vol. 4, p. 47.

[D 7050.]

"Hydrolysis of Cane Sugar by *d*- and *l*-Camphor-β-Sulphonic Acid."

By ROBERT JOHN CALDWELL, B.Sc., Clothworkers' Scholar, Chemical Department, City and Guilds of London Institute, Central Technical College. Communicated by Professor H. E. ARMSTRONG, F.R.S. Received June 16, 1904.

The study of the action of asymmetric hydrolytic agents on the sugars acquires interest from the fact that enzymes, which exhibit most remarkable activity as hydrolysts, are apparently all asymmetric in structure. The only experiments of the kind made hitherto are those by Emil Fischer,* on the action of *d*- and *l*-camphoric acids on cane sugar, described in his memoir on the importance to Physiology of Stereochemistry. No difference was detected: but as the experiments were made at 90° C. in sealed tubes, it was desirable to extend the inquiry and to operate under conditions more nearly comparable with those under which enzymes act.

At Professor Armstrong's suggestion, the acids selected for the purpose were the two isomeric acids of opposite activity prepared by direct sulphonation of *d*- and *l*-camphor by Reychler's method. They are easily prepared and they act quickly, so that their action can be studied at atmospheric temperatures; moreover, as concentrated solutions can be used, even a small difference in their activity should not escape detection. The inversion was carried out in a polarimeter tube enclosed in a jacket through which a flow of water was maintained varying in temperature by only ± 0·05° from 20·05° C. Readings of α_D were taken at intervals of 15 minutes. The results obtained are entered in the following tables, in which a is the amount of cane sugar per litre of solution when the first reading was taken and $a-x$ the concentration of the solution, at other times t minutes after the first reading. The strength of the acid in all cases was 0·488 gramme molecule per litre, as determined by titration with alkali. The concentration of the sugar solution used was 17·1 per cent. (0·5 gramme molecule). The rate of change was such that the inversion was about half completed at the end of six hours; the end point was determined in Cases I and II after 48 hours standing at 20° C.

Although there cannot have been any great difference in the conditions in the different experiments, the results must not all be included in one series, as the temperature regulator was readjusted after the first and after the fourth experiment; they are therefore to be considered in three sets, viz.: I: II, III, IV: V, VI, VII, VIII.

The first set gave K = 10·02 for the dextro acid and 9·95 for the lævo acid; in the second set, the value obtained for the dextro acid was 9·87, that for the lævo acid being 9·99.

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* 'Zeits. Physiol. Chem.,' 1898, vol. 26, p. 83.

Slight variations in the temperature would account for such differences, as the influence of temperature on the rate of change is known to be very great. But even in these experiments the variations observed are small and not such as to suggest any substantial difference between the two acids. In the last set of observations, fully set forth in the table on p. 187, which there is every reason to regard as satisfactory, there is clearly no evidence of a difference in the activity of the *d*- and *l*-acids to be noticed.

The results, therefore, not only confirm the conclusion arrived at by E. Fischer, but are also in agreement with the observations of Marckwald and Chwolles,* that methylic *d*- and *l*-tartrates are hydrolysed with equal readiness by *l*-nicotine (at 17·5 and 40° C.). On the other hand, they are in remarkable contrast with the conclusions of Marckwald and McKenzie† and of McKenzie‡ that ethereal salts similarly derived from optically active isomeric compounds are both formed and hydrolysed at different rates. It is to be noticed, however, that the experiments of these chemists were carried out at relatively high temperatures and that they involved racemisation.

An experiment made with chlorhydric acid and cane sugar under conditions precisely similar to those prevailing in Experiments V—VIII, using a solution containing 17·6 per cent. (0·5 gramme molecule) of cane sugar and 0·486 gramme molecule of hydrogen chloride, gave the value K = 11·18.

Representing the activity of hydrogen chloride as 100, that of camphor-β-sulphonic acid is therefore 89·8, which is a value in accord with that assigned by Ostwald to ethylsulphonic acid, viz., 91·2.

In the preliminary stage of the inquiry, a comparison was also made of the action of chlorhydric acid and of *d*-camphor-β-sulphonic acid on milk sugar at 60°·1. The value obtained for the former was K = 3·53.§ The values observed in the case of the camphor-acid were as follows:—

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* 'Ber.,' 1898, vol. 31, p. 783.

† 'Ber.,' 1899, vol. 32, p. 3120.

‡ 'Chem. Soc. Trans.,' 1904, vol. 85, p. 378.

§ 'Roy. Soc. Proc.,' vol. 73, p. 532.

18 per cent. (0·5 gramme molecule) milk sugar, 0·400 gramme molecule *d*-camphor-β-sulphonic acid. Temperature, 60°·1.

Time in hours.	α_D	Per cent. hydrolysed.	$\frac{10^4}{t}\log_{10}\frac{a}{a-x}$.
0	20·90	—	—
8	21·73	14·9	[1·46]
16	21·93	18·5	0·93
22	22·37	26·4	1·01
44	23·45	45·8	1·01
72	24·30	61·0	0·95
95	24·88	71·5	0·96
Complete change ...	26·47	Mean ...	0·97

K (for normal acid) = 2·43.

Although possibly affected by a considerable error, on account of the difficulty attending such observations at high temperatures, these results appear to indicate that the activities of the two acids are by no means the same towards cane sugar and towards milk sugar, being about 100 : 90 in the one case and 100 : 70 in the other. Sigmond has already shown* in the case of cane-sugar and maltose, that although sulphuric and oxalic acids have the same relative activity towards both carbohydrates, chlorhydric acid is relatively more active towards maltose: it appears, therefore, that cane sugar is less sensitive to attack by chlorhydric acid than are other sugars. The point is one which deserves further investigation.

Although the experiments described in this note have given a negative answer to the question considered, it is proposed to extend the inquiry to other acids.

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* 'Zeits. Phys. Chem.,' 1898, vol. 27, p. 390.

Time.	Dextro-acid.		Lævo-acid.		Dextro-acid.		Lævo-acid.	
	V.		VI.		VII.		VIII.	
	α_D.	$\frac{10^4}{t}\log_{10}\frac{a}{a-x}$.	α_D.	$\frac{10^4}{t}\log_{10}\frac{a}{a-x}$.	α_D.	$\frac{10^4}{t}\log_{10}\frac{a}{a-x}$.	α_D.	$\frac{10^4}{t}\log_{10}\frac{a}{a-x}$.
15	26·65	—	16·70	—	26·70	—	16·73	—
30	25·68	9·86	15·67	[10·45]	25·67	[10·46]	15·68	[10·65]
45	24·70	10·08	14·75	10·06	24·75	10·07	14·73	10·31
60	23·80	9·99	13·82	10·07	23·80	10·15	13·85	10·06
75	22·88	10·09	12·93	10·06	22·95	10·01	12·93	10·14
90	22·00	10·13	12·07	10·05	22·05	10·11	12·03	10·21
105	21·18	10·09	11·25	10·03	21·22	10·09	11·18	10·22
120	20·22	10·08	10·43	10·06	20·38	10·16	10·47	10·02
135	19·57	10·14	9·65	10·06	19·65	10·07	9·67	10·06
150	18·88	10·04	8·88	10·09	18·85	10·14	8·92	10·06
165	18·15	10·05	8·18	10·05	18·17	10·07	8·18	10·08
180	17·45	10·05	7·47	10·06	17·45	10·10	7·50	10·05
195	16·75	10·08	6·82	10·03	16·72	10·16	6·82	10·05
210	16·12	10·06	6·17	10·03	16·07	10·16	6·17	10·05
225	15·48	10·07	5·47	10·11	15·40	10·15	5·57	10·01
240	14·85	10·08	4·92	10·04	14·80	10·18	4·93	10·05
255	14·27	10·08	4·32	10·05	14·22	10·17	4·33	10·06
270	13·65	10·14	3·73	10·07	13·67	10·15	3·83	9·99
285	13·12	10·12	3·20	10·05	13·15	10·11	3·25	10·02
300	12·60	10·11	2·73	9·99	12·53	10·20	2·70	10·04
315	12·05	10·14	..	..	12·05	10·17	2·22	10·00
345	..	..	1·18	10·06	..	..	..	..
Complete change	− 2·33	..	−12·35	..	− 2·33	..	−12·35	..
Mean	..	10·07	..	10·05	..	10·13	..	10·08

[D 1850, 7050, 8010.]

"Studies on Enzyme Action. V.—Hydrolysis of Isomeric Glucosides and Galactosides by Acids and Enzymes."

By EDWARD FRANKLAND ARMSTRONG, Ph.D., Salters' Company's Research Fellow, Chemical Department, City and Guilds of London Institute, Central Technical College. Communicated by Professor H. E. ARMSTRONG, F.R.S. Received August 26, 1904.

In view of the use constantly made, in contrasting the action of sucroclastic enzymes, of the stereoisomeric α- and β-methyl glucosides and the corresponding galactosides as test materials, it was desirable to gain some idea of the relative stability of these four compounds in presence of acids and wherever possible towards enzymes, a knowledge of their behaviour being of importance, both as throwing light on their intrinsic properties and for the purpose of correlating the activities of the various compounds amenable to hydrolysis.

As already pointed out,* in studying the hydrolysis of sugars under the influence of enzymes, it is difficult to institute just comparisons, as not only, as a rule, is a different enzyme required for each sugar, but we have no means at present of determining the amount of enzyme used; and sooner or later, it will be necessary to accumulate data correlating one or more analytical factors (nitrogen percentage, etc.) with hydrolytic activity. The difficulty spoken of is enhanced by the fact that, usually, several enzymes occur together—so that no ordinary analytical process can suffice for the determination of the amount of a particular enzyme present in a solution.

On the other hand, it will be of importance to determine whether any one enzyme is capable of hydrolysing several different compounds or whether each particular hydrolysis is ascribable to some one particular enzyme. There is only one case at present known which can be discussed with any degree of certainty. It has been urged by some French workers, especially by Bourquelot and Herissey,† that the action of emulsin on milk sugar, is due to the presence of small quantities of lactase, together with the emulsin proper. The following facts, brought forward in Nos. 2 and 3 of this series of papers, may, however, be urged against this view.

(1) The curve expressing the rate at which milk sugar changes is not of the form to be expected if only a very small quantity of enzyme (lactase) were present: in that case a linear expression should apply during the early stages; actually the curve is only of this form when small quantities of emulsin are used.

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* 'Roy. Soc. Proc.,' 1904, vol. 73, p. 515.

† 'Compt. Rend.,' 1903, vol. 137, pp. 56, 59.

(2) The action of emulsin on milk sugar is most retarded by glucose, and only to a slight extent by galactose, whereas galactose alone affects the action of lactase. This, again, would appear to afford proof that the emulsin is directly active.

(3) The curves for emulsin fall off very much more rapidly than those for lactase, showing that the action of the products in removing the enzyme is greater in the former case.

It therefore appears that the differences apparent in the behaviour of emulsin and lactase towards milk sugar are such as to render it improbable that the action of the emulsin is due to the presence of a small proportion of lactase; it would seem, rather, that emulsin is capable of acting on β-galactosides as well as on β-glucosides.*

A different enzyme being required, as a rule, for each sugar, the relative activities of enzymes cannot well be reported in terms of any particular sugar taken as standard; the only method open to us at present is to determine the activity of a particular acid towards the various sugars and to estimate, by direct comparison, the activity of the enzyme in terms of this standard acid. But, unfortunately, acids compare very unfavourably with enzymes as hydrolysts: so that, in order to effect hydrolysis at any reasonable rate, it is necessary, except in the case of cane sugar, to operate at elevated temperatures, at which a direct comparison between acid and enzyme is impossible. The experiments here described are to be regarded merely as a first attempt in the direction indicated.

Acid Activity.—The method adopted is substantially that previously described. Solutions of the glucoside containing 3 grammes per 100 c.c. were hydrolysed by means of a half gramme molecular proportion of hydrogen chloride at 74°. The following tables give the results obtained with the various hexosides. The values of the velocity constant K, expressed in the last column, are calculated on the assumption that the change is mono-molecular.

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* Pottevin's ('Ann. Inst. Pasteur,' 1903, vol. 17, p. 31) investigations seem to show, however, that *Aspergillus niger* contains an enzyme which is capable of hydrolysing β-glucosides but not β-galactosides or milk sugar. It remains an open question whether this "emulsin" is identical with that obtained from almonds.

Table I. Table II.

α-Methyl glucoside.

Temperature, 74°·1.			Temperature, 74°·8.		
Time in hours.	Change in rotation = x.	$K = \frac{1}{t}\log\frac{a}{a-x}$.	Time in hours.	x.	K.
	mins.			mins.	
2	15	0·00955	2	18	0·0115
4	30	0·00975	4	34	0·0111
7	52	0·01000	6	48	0·0107
17·5	117	0·01010	24	174	0·0124
21	137	0·01027			
24	146	0·00977			
29	176	0·01047			
Total change	$a = 350$	Mean K = 0·01		$a = 350$	K = 0·0114

Table III. Table IV.

β-Methyl glucoside.

Temperature, 74°·1.			Temperature, 74°·8.		
Time.	x.	K.	Time.	x.	K.
	mins.			mins.	
1	11	0·0177	2	28	0·0238
2	22	0·0181	4	50	0·0218
4	41	0·0178	6	70	0·0213
6	60	0·0178	24	193	0·0219
7	69	0·0179	48	253	0·0228
	$a = 275$	K = 0·0179		$a = 275$	K = 0·0220

Table V.
α-Methyl galactoside.

Table VI.
β-Methyl galactoside.

Temperature, 74°·1.			Temperature, 74°·8.		
Time.	x.	K.	Time.	x.	K.
	mins.			mins.	
2	72	0·0537	2	42	0·1068
4	125	0·0518	4	85	0·1059
5	150	0·0528	5½	105	0·1041
7	196	0·0562	7	121	0·1077
10	240	0·0567			
	a = 329	K = 0·0542		a = 154	K = 0·1061

Table VII. Table VIII.
Salicin. Temperature, 74°·1.

t.	x.	K.	t.	x.	K.
	mins.			mins.	
1	48	0·0612	0·5	26	0·0642
2	85	0·0576	1·5	65	0·0535
3	124	0·0601	2·5	105	0·0589
4	161	0·0632	3·5	141	0·0606
6	205	0·0597	5·5	199	0·0622
8	244	0·0600	7·5	235	0·0598
	a = 365	mean 0·0603		a = 365	mean 0·0599

The mean values of K are collected in the following table, which also contains Sigmond's value* for maltose :—

Table IX.

Hexoside.	$K = \frac{1}{t} \log \frac{a}{a-x}$.	
	Temperature, 74°·1.	Temperature, 74°·8.
α-Methyl glucoside	0·0100	0·0114
β-Methyl glucoside	0·0179	0·0220
α-Methyl galactoside	0·0542	0·0650*
β-Methyl galactoside	0·0884*	0·1061
Salicin..........................	0·0601	
Maltose..........................	0·0740	

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* 'Zeit. Phys. Chem.,' 1898, vol. 27, p. 385.

It will be noticed that the various hexosides vary widely in stability: the β-glucosides undergoing hydrolysis more rapidly than the stereoisomeric α-compounds—a fact already noted by Alberda von Ekenstein—whilst the galactosides are more rapidly attacked than the corresponding glucosides. These conclusions are in harmony with the well-known fact that the α-compound preponderates in the mixtures obtained in preparing the methyl glucosides and galactosides[*] and also serve to explain the circumstance that, in separating methyl galactoside (by E. Fischer's method), it is necessary to avoid the presence of acid far more carefully than in separating methyl glucoside.

In the case of the α- and β-glucosides and galactosides, the stereoisomerism in each pair of compounds is confined to the terminal carbon atom; it is, perhaps, noteworthy that there should be so considerable a difference between compounds so related.

But it is even more surprising that a change in the general configuration at the fourth carbon atom, affecting only the nature of the attachment of the oxygen atoms within the ring, such as occurs when glucose passes into galactose, should have so marked an influence on the activity of the group associated with the terminal carbon atom. Such a result enhances the probability of the conclusion that the active system within which the change takes place[†] is formed by the association of acid-water molecules with the oxygen atom in the pentaphane ring: in other words, that this oxygen atom is the attractive centre. The argument here made use of renders it desirable that the behaviour of the isomeric mannosides towards acids should also be studied, in order that it may be possible eventually to define more or less accurately the functions of the different oxygen atoms in the molecule.

Enzyme Activity.—At present, the experiments have been confined to two substances, maltose and α-methyl glucoside, which both undergo hydrolysis under the influence of the enzymes contained in ordinary yeast maltase.

Fifty cubic centimetres of a solution containing 5 grammes of α-methyl glucoside was mixed with 50 c.c. of a maltase extract prepared from dried yeast;[‡] the mixture was kept at 22°. Samples were withdrawn every hour and polarimetrically examined. Considerable difficulty was at first experienced in obtaining sufficiently clear solutions for this purpose, owing to the impossibility of removing the suspended proteid matter by mere filtration; it was eventually discovered that the liquids could be clarified by means of sodium acetate. The method at present adopted consists in mixing 5 c.c. of water at 100°, containing 0·5 gramme of sodium acetate, with the 5 c.c. withdrawn, then shaking with charcoal and filtering through a double filter.

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[*] E. Fischer, 'Ber.,' vol. 26, p. 2400; Jungius, 'Proc. K. Akad. Wetensch.,' Amsterdam, 1903, vol. 6, p. 99.

[†] Compare Armstrong and Caldwell, 'Roy. Soc. Proc.,' vol. 73, p. 526.

[‡] 'Roy. Soc. Proc.,' vol. 73, p. 504.

Table X.

Time in hours.	Percentage changed = x.	$K = \frac{1}{t} \log \frac{100}{100-x}$.
	mins.	
1	8·7	0·0395
2	16·6	0·0394
3	24·0	0·0397
4	31·3	0·0407
5	37·0	0·0401

To effect a direct comparison of the activity of maltase towards maltose and α-methyl glucoside, the two substances were hydrolysed by the same yeast extract under precisely similar conditions. The extract used in this case was prepared by digesting 5 grammes of dried yeast with 100 c.c. of water at 22° during 1 hour.

Table XI.

Time in hours.	α-Methyl glucoside.		Maltose.	
	x.	K.	x.	K.
	mins.		mins.	
1	5·55	0·0248	21·2	0·098
2	10·5	0·0241	36·0	0·0969
3	14·8	0·0232	43·0	0·0814
4	18·5	0·0222	49·4	0·0722
5	22·2	0·0218	53·6	0·0667
6	25·9	0·0217	58·2	0·0631

It will be seen that the maltose was hydrolysed very much more quickly than the α-methyl glucoside. In both cases the velocity coefficient K diminishes as action proceeds; but to a far greater extent in the case of maltose. This difference is obviously due to the different influence exercised by the products of change in the two cases. It is to be remembered that two molecules of glucose are produced by the hydrolysis of maltose but only one from α-methyl glucoside; any retardation, therefore, which glucose can effect should be less obvious in the case of the glucoside.

On comparing the results recorded in the above tables with those given on pp. 190—191, representing the action of acid, it is obvious that the enzyme was much more active than the acid. About 40 per cent. of the glucoside was changed in 5 hours at 22° by the enzyme; whereas, when acid was used, even in so large a proportion as three molecules of hydrogen chloride to one of glucoside, the same amount of change was effected in only about 20 hours at 75°. As the enzymes are undoubtedly of high molecular weight and the proportion of maltase in the yeast extract is certainly small, it would seem to follow that the relative molecular activity of the enzyme is very great compared with that of the acid. But, as pointed out in an earlier paper,* inasmuch as only a small proportion of the acid is actually active, it is probable that the enzyme owes its apparent activity to its greater affinity for the sugar and that, in reality, the acid has the greater hydrolytic activity.

On account of the rapid alteration in the values of K, it is difficult to make any exact numerical comparison between maltose and methyl glucoside. The initial value of K, in the case of the glucoside, may be estimated at about 0·025; in view of the results previously obtained,† which throw considerable light on the behaviour of maltose during the early stages of hydrolysis, the corresponding value for this sugar may be set at 0·12 or even higher. Comparing these initial rates, it would appear that maltose is hydrolysed from five to six times as rapidly as α-methyl glucoside, a result of the same order as that deduced in comparing the action of chlorhydric acid on the two hexosides.

Taking into account both the superior stability of the methyl glucoside and the greater influence exercised by the products of change in the case of maltose, the difference in the behaviour of the two compounds on hydrolysis seems to be satisfactorily accounted for.

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* Part 4, *loc. cit.*

† 'Roy. Soc. Proc.,' vol. 73, p. 508.

[D 7050, 8010.]

"Studies on Enzyme Action. VI.—The Sucroclastic Action of Acids as contrasted with that of Enzymes. Part II."

By Edward Frankland Armstrong, Ph.D., Salters' Company's Research Fellow and Robert John Caldwell, Clothworkers' Scholar, Chemical Department, City and Guilds of London Institute, Central Technical College. Communicated by Professor H. E. Armstrong, F.R.S.

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D 7050. *Hydrolysis of Cane Sugar by very Dilute Acids.*

In accordance with the theory put forward in our former paper,[*] it was to be expected that on hydrolysing cane sugar with sufficiently dilute acids the course of the change would not follow the simple logarithmic law but that it would approximate, during the earlier period, to a linear function of the time. This supposition has been confirmed by experiments made very carefully to test this point.

Experimental Method:—In order that hydrolysis should be about half completed in 10 hours by N/500 chlorhydric acid, it was necessary to work at about 40°. At this temperature, when so weak an acid is used, the solution does not show any trace of colour even after 4 days, which may be regarded as evidence that no decomposition of the levulose into acid substances has occurred. In order to maintain the temperature at 40°, a stream of water was passed through the jacket of the polarimeter tube in which the hydrolysis was carried out. The water was taken from the mains at nearly 18° and passed through a metal vessel, about 2 litres in capacity, in which it was heated by a Bunsen burner to 30°. It was then passed through a metal vessel holding about 5 litres containing an Ostwald thermoregulator; in this the temperature of the water was raised to about 39°. The final adjustment was performed by a very sensitive Ostwald thermoregulator with fluted sides to make it respond quickly to changes in temperature; this was placed in a cylindrical Dewar vacuum vessel, which it almost filled. After passing through a thin copper drum holding about 150 c.c., the water circulated through the regulator, cooling being prevented by the vacuum jacket; the temperature of the water in the drum was maintained at 40° by means of a flame controlled by the regulator. This arrangement proved to be eminently satisfactory in observing slow rates of change, although the extreme variation of the temperature was nearly ± $\frac{1}{10}$th of a degree, the period of the variations was only 1 minute, so that in experiments extending over several hours the temperature variation was of no account.

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[*] 'Roy. Soc. Proc.,' vol. 73, p. 526.

The strength of the acid selected was N/500 hydrogen chloride; the two sugar solutions used contained 171 and 342 grammes sucrose per litre. The polarimeter tube had been in use for a considerable time with acid solutions. The solutions of sugar and acid were accurately measured out from burettes into a small flask into which steam had been passed, according to Ostwald's directions, to free it from alkali. The mixture was then rapidly filtered into the polarimeter tube. The first reading was taken 10 or 15 minutes after mixing, when the temperature had attained to that of the thermostat.

As under these conditions the rotatory power of the solution fell quickly, the polarimeter readings had to be taken very rapidly, so that the possible error in the tabulated values (although amounting to only 0·1 per cent.) is about 0·03°, making a possible error of 3 units in the third column of differences.

By taking a very large number of points, such minor errors are eliminated and when the velocity constant K is calculated according to the usual logarithmic law a very steady series of values is obtained.

From Tables I—IV it will at once be obvious that the value of the velocity coefficient K steadily increases during about the first 4 or 5 hours of the change and then remains constant, the figures obtained being in striking contrast with those of Ostwald and also with those given later in this paper, Tables VI, VII, for experiments in which stronger solutions of acid were used: in all these experiments the successive values of K vary up and down on either side of a mean value.

The fact that the value of K rises is an indication that change proceeds faster than the mass-action law requires. On the other hand, the figures do not offer definite evidence that the change proceeds at a strictly linear rate, although in all cases, especially that recorded in Table II, the approximation to a straight line law during the first 2½ hours is very close: indeed, if the possible error in the difference be taken into account, the first 10 or 15 per cent. of the change is practically linear. When the values are plotted on rectangular co-ordinates, the curve obtained falls between the straight line and the mass-action curve.

Furthermore, Tables III and IV indicate that the approximately linear portion of the change persists the longer the larger the proportion of sugar to acid.

It is obvious from these results that the analogy between acid and enzyme action is complete. In both cases, when the proportion of hydrolyst is relatively small the change is at first approximately a linear function of the time and subsequently a logarithmic function; whilst when a larger proportion of hydrolyst is present, the change is from the first a logarithmic function which may become modified by secondary causes. The association theory of hydrolysis put forward in

	Table I.			Table II.		
Time in minutes.	α_D.	Average difference per 30 minutes.	K.	α_D.	Average difference per 30 minutes.	K.
0	22·22	..	..	22·12	..	..
15	21·83	..	412	21·73	..	414
30	21·40	82	437	21·35	77	411
45	21·00	..	437	20·97	..	412
60	20·63	81	430	20·58	76	417
75	20·18	..	445	20·22	..	415
90	19·77	80	449	19·82	77	422
105	19·45	..	438	19·45	..	423
120	19·00	80	449	19·03	76	431
135	18·63	..	448	18·72	..	425
150	18·27	72	447	18·37	69	425
165	17·92	..	446	18·00	..	427
180	17·52	75	451	17·60	77	433
195	17·18	..	449	17·23	..	436
210	16·83	70	450	16·90	67	435
225	16·47	..	451	16·60	..	438
240	16·17	68	448	16·27	65	433
255	15·78	..	453	15·93	..	434
270	15·43	73	454	15·60	66	435
285	15·05	..	459	15·27	..	437
300	..	..	..	14·93	65	439
315	..	..	..	14·63	..	438
330	..	..	..	14·30	65	441
345	13·87	54	455	13·95	..	444
360	13·57	..	454	13·68	61	442
375	13·25	62	455	13·35	..	445
390	12·95	..	456	13·10	55	443
405	12·65	57	457	12·83	..	442
420	12·42	..	454	12·53	58	444
435	12·13	55	454	12·23	..	445
450	11·85	..	453	11·97	53	445
465	11·58	54	455	11·73	..	443
480	11·32	..	455	11·48	50	448
495	11·07	52	454	11·23	..	443
510	10·80	..	455	11·03	45	440
525	10·58	49	453	..	..	..
Complete change	−5·37	..	..	−5·37	..	..

	Table III.			Table IV.		
Time in minutes.	α_D.	Average difference per 30 minutes.	K.	α_D.	Average difference per 30 minutes.	K.
0	46·03	..	..	44·63	..	..
10	45·47	..	428	44·02	..	481
20	44·83	..	461	43·37	..	489
30	44·20	..	471	42·75	..	493
40	43·62	185	468	42·20	183	487
50	42·97	..	478	41·58	..	492
60	42·37	..	479	40·93	..	500
70	41·80	182	477	40·30	186	505
80	41·17	..	482	..	..	..
90	40·57	..	485	39·10	..	507
100	40·07	175	488	38·47	183	512
110	39·45	..	483	37·87	..	513
120	38·85	..	486	37·28	..	515
130	38·28	176	487	36·70	178	516
140	37·67	..	491	36·13	..	516
150	37·18	..	490	35·53	..	519
160	36·55	173	492	34·95	177	521
170	36·03	..	491	34·33	..	525
180	35·43	..	495	33·78	..	526
190	34·93	167	494	33·25	168	525
200	34·45	..	492	32·73	..	525
210	33·87	..	495	32·25	..	523
220	33·38	156	494	31·65	158	527
230	32·87	..	494	31·13	..	527
240	32·38	..	494	30·65	..	526
250	..	152	..	30·13	154	527
260	31·28	..	499	29·62	..	528
270	30·80	..	499	29·08	..	530
280	30·38	154	496	28·60	152	530
290	29·87	..	498	28·15	..	529
300	29·48	..	495	27·63	..	530
310	28·83	144	502	27·22	142	528
320	28·42	..	500	26·72	..	530
330	27·93	..	501	26·28	..	529
340	27·43	146	503	25·83	138	529
350	26·97	..	503	25·32	..	532
360	26·55	..	503	24·88	..	533
370	26·12	134	503	24·47	135	531
380	25·65	..	504	24·02	..	532
390	25·25	..	504	23·60	..	531
400	24·87	126	502	23·15	130	532
410	24·42	..	503	22·73	..	532
420	24·02	..	503	22·35	..	531
430	23·62	124	503			
440	23·17	..	504			
450	22·80	..	503			
460	22·38	128	504			
470	21·93	..	506			
480	21·53	..	507			
490	21·13	123	507			
500	20·77	..	507			
510	20·40	..	507			
520	20·00	112	508			
530	19·68	..	506			
540	19·27	..	508			
Complete change..	−11·12	..	..	−10·79		

these papers gives a very satisfactory explanation of the observed phenomena; as before stated, the differences between acid and enzyme action can all be attributed to the crystalloid nature of the former and the colloid nature of the latter.

Influence of the Products of Change.—In view of the theoretical importance of the influence of the products of change,* it appeared desirable to extend our experiments in this direction to cane sugar. Accordingly the effect of adding 9 grammes of glucose or fructose to 100 c.c. of 17·1 per cent. sucrose containing half a gramme molecule of hydrogen chloride has been determined in the manner previously described by one of us for β-camphor sulphonic acid at 20°.

The results are incorporated in the following tables:—

	Table V.		Table VI.		Table VII.	
Time.	17·1 grammes sucrose per 100 c.c.		17·1 grammes sucrose per 100 c.c.		17·1 grammes sucrose + 9·0 grammes glucose per 100 c.c.	
	α_D.	$\frac{10^4}{t}\log\frac{a}{a-x}$.	α_D.	$\frac{10^4}{t}\log\frac{a}{a-x}$.	α_D.	$\frac{10^4}{t}\log\frac{a}{a-x}$.
0	+21·55	..	+21·62	..	+30·72	..
15	20·40	[11·83]	20·42	[12·32]	29·53	[10·93]
30	19·30	[11·81]	19·47	11·23	28·37	12·37
45	18·27	11·70	18·48	11·14	27·22	12·55
60	17·33	11·50	17·48	11·23	26·17	12·50
75	16·40	11·44	16·55	11·21	25·25	12·25
90	15·43	11·56	15·53	11·46	24·25	12·34
105	14·60	11·45	14·70	11·37	23·33	12·32
120	13·75	11·46	13·90	11·29	22·38	12·43
135	12·95	11·44	13·12	11·25	21·45	12·55
150	12·10	11·55	12·35	11·25	20·67	12·49
165	11·37	11·51	11·53	11·35	19·87	12·51
180	10·65	11·51	10·87	11·27	19·10	12·53
195	9·93	11·54	10·13	11·34	18·30	12·63
210	9·30	11·49	9·42	11·39	17·65	12·57
225	8·62	11·54	8·90	11·25	17·03	12·52
240	8·02	11·52	8·25	11·29	16·42	12·49
Complete change	−7·18	..	−7·18	..	+2·03	..
	Mean ..	11·52	Mean ..	11·29	Mean ..	12·47

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* *Loc. cit.*, p. 534.

Table VIII. Table IX. Table X.

Time.	17·1 grammes sucrose + 9·0 grammes glucose per 100 c.c.		17·1 grammes sucrose + 9·0 grammes fructose per 100 c.c.		17·1 grammes sucrose + 9·0 grammes fructose per 100 c.c.	
	α_D.	$\frac{10^4}{t} \log \frac{a}{a-x}$.	α_D.	$\frac{10^4}{t} \log \frac{a}{a-x}$.	α_D.	$\frac{10^4}{t} \log \frac{a}{a-x}$.
0	+ 30·63	..	+ 4·35	..	+ 4·24	..
15	29·45	12·20	3·18	12·07	3·13	12·59
30	28·25	12·58	2·03	12·22	1·97	12·55
45	27·13	12·60	+ 0·95	12·19	+ 0·92	12·31
60	26·15	12·33	− 0·10	12·22	− 0·10	12·22
75	25·12	12·39	1·08	12·17	1·10	12·22
90	24·12	12·46	2·05	12·20	2·13	12·37
105	23·15	12·54	2·97	12·20	3·05	12·26
120	22·23	12·58	3·85	12·20	3·90	12·29
135	21·33	12·65	4·70	12·21	4·82	12·41
150	20·45	12·74	5·55	12·27	5·65	12·43
165	19·67	12·72	6·30	12·23	6·43	12·43
180	19·00	12·59	7·07	12·27	7·20	12·45
195	18·18	12·73	7·82	12·32	7·93	12·47
210	17·48	12·73	8·48	12·28	8·63	12·48
225	16·80	12·75	9·07	12·20	9·25	12·43
240	16·13	12·80	9·77	12·29	9·93	12·49
Complete change	+ 2·03	..	−24·30	..	−24·30	..
	Mean ..	12·59	Mean ..	12·22	Mean ..	12·38

Calculating from the equation

$$K = K_1 [1 + 0{\cdot}0131\ \rho]$$

given by Arrhenius as that expressing the influence of concentration ρ on the constant of hydrolysis, it follows that in the case of a solution containing 17·1 + 8·55 grammes of cane sugar per 100 c.c.,

$$K = 12{\cdot}45$$

The results obtained may thus be summarised—

Table XI.

			Mean value of K.
(i)	9·0 grammes	glucose	12·53
(ii)	9·0 „	fructose	12·30
(iii)	9·0 „	invert sugar (mean of (i) and (ii))	12·42
(iv)	8·55 „	cane sugar (calc.)	12·45

It will be seen that about the same increase in the value of K is produced by equimolecular proportions of glucose and fructose, whilst the molecular effect of the biose cane-sugar is about twice the molecular effect of the monose.

The acceleration brought about by the addition of sugars may be attributed to a withdrawal of water by the sugar and the consequent increase in the amount of the "active system," as pointed out in our previous paper.

"Studies on Enzyme Action: The Effect of 'Poisons' on the Rate of Decomposition of Hydrogen Peroxide by Hæmase." By GEORGE SENTER, Ph.D., B.Sc. (Lond.). Communicated by Professor E. H. STARLING, F.R.S. Received June 2, 1904.

Schönbein[*] was the first to observe that most animal and vegetable juices have the property of decomposing hydrogen peroxide into water and oxygen, as well as the power of developing a blue colour in tincture of guaiacum containing a little hydrogen peroxide. Since these properties belonged to all the enzymes then known, *e.g.*, emulsin and diastase, Schönbein regarded them as characteristic of enzymes in general, and used them in his numerous investigations as tests for the presence of these bodies.

A good many years afterwards Jacobson,[†] working with impure emulsin and pancreatin, showed that the power of these enzymes to catalyse hydrogen peroxide could be destroyed without affecting seriously the specific ferment action. A year or two ago, Loew[‡] suggested that the power of plant and animal juices to decompose hydrogen peroxide is due to an enzyme of very wide distribution, which he has named catalase. According to this view, Jacobson's impure emulsin contained some catalase, which is less resistant against heat than the emulsin, and can be rendered inactive without affecting seriously the other ferment.

Since Schönbein's time, the properties which blood possesses of decomposing hydrogen peroxide and of giving the guaiacum reaction have formed the subject of numerous investigations by Schmidt,[§] Bergengrün,[||] Spitzer,[¶] Schär,[**] Cotton,[††] Ville and Moitessier,[‡‡] and others, and this is not surprising when we consider the importance of the guaiacum test for the detection of small amounts of blood.

Spitzer[§§] concluded that the guaiacum reaction and the catalysis of hydrogen peroxide are due to the same substance, and this has been the generally accepted opinion* until very recently. Schmidt long ago suggested that the catalysis of hydrogen peroxide by blood is due to the hæmoglobin, and though this view had been combated by Kobert,† Schär,‡ and others, no very definite evidence had been brought forward on either side.

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[*] 'Journ. f. prakt. Chemie,' vol. 89, p. 334 (1863).

[†] 'Zeit. f. physiol. Chemie,' vol. 16, p. 340 (1892).

[‡] Loew, "Catalase," 'U.S. Dept. of Agriculture Report,' No. 68, 1901.

[§] Pflüger's 'Archiv,' vol. 6, p. 413 (1872).

[||] 'Inaug. Dissertation,' Dorpat, 1888.

[¶] Pflüger's 'Archiv,' vol. 67, p. 615 (1897).

[**] 'Zeit. für Biologie,' vol. 6, p. 467 (1870).

[††] Cotton, 'Bull. Soc. Chim.,' vol. 25, p. 255 (1901).

[‡‡] 'Bull. Soc. Chim.' [3], vol. 27, p. 1003 (1902).

[§§] *Loc. cit.*

Last year the author§ succeeded in preparing from defibrinated ox blood a body which energetically decomposes hydrogen peroxide and does not give the guaiacum reaction. This body, which has so far been obtained only in solution, has been named hæmase.

In the former paper‖ it has been shown that hæmase rapidly loses its activity when heated in dilute aqueous solution to 60°; that in moderately dilute hydrogen peroxide solutions hæmase undergoes slow oxidation by the peroxide simultaneously with the catalysis of the latter, but that in dilute ($n/100$) peroxide solutions the latter is split up without the catalysor being affected. It has also been shown that in dilute solution the velocity of the decomposition of the peroxide is, within fairly wide limits, proportional to the hæmase concentration and to the concentration of the hydrogen peroxide. Preliminary investigation of the effect of other substances on the reaction showed that it is greatly retarded by very small amounts of acids and alkalis and to a much smaller extent by sodium chloride.

As regards the nature of the catalysor in question there seems good reason to regard it as belonging to that rather indefinite class of substances known as enzymes. In the present state of our knowledge no good definition of an enzyme can be given. We may regard them as substances formed by living cells which can be separated from the latter without losing their activity, and under whose influence certain chemical changes are brought about in a catalytic manner. They are soluble in water, precipitated by alcohol, destroyed by heating in aqueous solution to 60° or 70°, and their activity is often greatly influenced by small traces of foreign bodies. In all respects hæmase conforms to the above definition.

Since hæmase (in aqueous solution at 0°) is exceedingly stable and the velocity measurements are so accurately reproducible on different occasions (remarkably so for an enzyme action), the investigation has been continued with the hope of throwing some light on the nature of the enzyme, and the present communication contains an account of the influence of various substances on the rate of reaction.

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* *Vide* Oppenheimer, 'Fermente,' p. 45.

† 'Naturforscherversammlung Aachen,' 1900, quoted by Bredig, 'Anorganische Fermente,' Leipzig, 1901, p. 88.

‡ 'Zeit. fur Biologie,' vol. 19, p. 380 (1899).

§ 'Zeit. für physik. Chemie,' vol. 44, p. 257 (1903).

‖ Senter, *loc. cit.*

Method of Measuring the Reaction Velocity.

All the experiments mentioned in the present communication were carried out in a thermostat at a temperature of 10° (constant to $\frac{1}{10}^{\circ}$). Ninety cubic centimetres of the very dilute enzyme solution was placed in each bottle, 10 c.c. of a solution of the substance whose action was to be investigated (respectively 10 c.c. of water in the control experiments) added; after the lapse of a certain time (period of incubation) 100 c.c. of approximately *n*/50 hydrogen peroxide (also at 10°) added, and the mixture shaken. From time to time 25 c.c. of the mixture were pipetted out, run into sulphuric acid, which stops the action, and titrated with *m*/500 permanganate.

It may be mentioned that the enzyme solution was so active, compared with the amount of organic matter present, that no appreciable error (less than $\frac{1}{10}$ c.c.) was caused through the reduction of $KMnO_4$ by organic matter. The hydrogen peroxide used was obtained from Merck and was quite pure.

The enzyme solution was prepared according to the method given in my former paper,* and being kept in an ice-box retained its activity without appreciable change for several days.

Nearly all the substances used in the experiments were obtained from Kahlbaum, the others were the purest obtainable in London.

The water used for dilution was distilled water freed from carbon dioxide by the passage of a current of pure air through it for some time.

Effect of Acids on the Reaction Velocity.

In order to show clearly the nature of the results obtained, I give here (p. 204) full details of measurements on the effect of HCl, H_2SO_4, and HNO_3 on the reaction-velocity. In order to economise space, only the "constants" of subsequent experiments will be given.

The value of the constant in the control experiment was 0·0250. The numbers under $C_{H_2O_2}$ give the concentration of the H_2O_2 at the time indicated, expressed in cubic centimetres of 1/500 molar $KMnO_4$. The constants in the third column are calculated on the assumption that the reaction-velocity is proportional to the H_2O_2 concentration, that is, that $-\frac{dC_{H_2O_2}}{dt} = K_1C_{H_2O_2}$ where $C_{H_2O_2}$ is the concentration at the time t. Integrating, we obtain $0·4343K_1 = \frac{1}{t_2 - t_1}\log\frac{C_1}{C_2}$, where C_1 and C_2 are two successive measurements, and $t_2 - t_1$ the interval of time between them.

The effect of hydrochloric acid, sulphuric acid, nitric acid, benzoic acid, succinic acid, and acetic acid, on the rate of reaction has been

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* *Loc. cit.*

Table I.—Initial Concentration of H_2O_2 in the Reaction Mixture approx. *n*/200.

t (min.).	$C_{H_2O_2}$.	0·4343K_1.	*t* (min).	$C_{H_2O_2}$.	0·4343K_1.
HCl *n*/40,000.			HCl *n*/100,000.		
0	22·7	—	0	22·7	—
8·5	19·8	0·0070	8	17·3	0·0147
23·5	15·5	0·0071	23	10·3	0·0150
39·5	11·8	0·0074	38	6·2	0·0150
68·5	7·4	0·0070	53	3·7	0·0150
HNO_3 *n*/40,000.			HNO_3 *n*/100,000.		
0	22·7	—	0	22·7	—
105	21·2	0·0003	41	19·1	0·0018
225	19·2	0·0003	71	16·7	0·0019
			130	12·6	0·0020
			250	7·0	0·0021
			405	3·1	0·0022
H_2SO_4 *n*/40,000.			H_2SO_4 *n*/100,000.		
0	22·7	—	0	22·7	—
10	19·5	0·0066	9	16·7	0·0148
25	15·1	0·0074	24	9·9	0·0151
40	11·8	0·0071	39	5·9	0·0150
70	7·1	0·0073	54	3·5	0·0150
130	2·8	0·0068	—	—	—

investigated. Results for the first three acids have been given above; the following are the results obtained for the other three, with the numbers for HCl, obtained at the same time, for the sake of comparison :—

Table II.

Concentration of acid.	Concentration of H-ions.	Constants.
Acid, hydrochloric, *n*/10,000	*n*/10,000	0·0015
„ „ *n*/20,000	*n*/20,000	0·0034
„ benzoic, *n*/4,000	*n*/11,000	0·0019
„ „ *n*/10,000......	*n*/19,000	0·0033
„ „ *n*/25,000......	*n*/37,000	0·0078
„ succinic, *n*/10,000......	*n*/18,200	0·0029
„ „ *n*/25,000......	*n*/36,000	0·0070
„ acetic, *n*/1,333	*n*/10,000	0·0041
„ „ *n*/2,666	*n*/13,000	0·0049
Control experiment	0	0·0300

From the tables, it will be seen that, while HCl and H_2SO_4, which are completely dissociated under the conditions of experiment, give exactly the same retardation, benzoic, succinic, and acetic acids, which are only partly dissociated, have considerably less effect in equivalent concentration; when, however, the concentration in hydrogen ions is calculated (see second column), HCl, H_2SO_4, benzoic acid and succinic acid have exactly the same retarding effect, that is, the retardation is proportional to the hydrogen ion concentration. Nitric acid is more, and acetic acid less, poisonous than would be expected from the hydrogen ions present, and it is natural, in these two cases, to suggest that the negative ions exert an influence. This has been shown to be the case, as will be mentioned more fully later. While the Cl and SO_4 ions exert comparatively little influence, potassium nitrate slows down the action to about the same extent as nitric acid itself. On the other hand, sodium acetate has more accelerating influence on the reaction than any other substance that has been tried.

I may here mention that, although from considerations of space only one series of results has been given, three series of measurements have been carried out at different times with different enzyme preparations, and exactly corresponding results obtained, so that the figures quoted may be accepted as reliable.

Another interesting point about the behaviour of acids is that the time during which the acid remains in contact with the enzyme before the H_2O_2 is added has no influence on the result; the equilibrium is attained within 5 minutes, and remains unaltered at the end of 2 or 3 hours. The change is not a permanent one, since if the acid, after an incubation period of 2 hours, be neutralised before the addition of the H_2O_2, the action proceeds with its original velocity.

Kahlenberg* and his assistants have made a systematic investigation of the toxic action of acids on small plants and on fishes, with the object of finding whether the electrolytic dissociation theory is capable of explaining the results. They find that the toxic effect is in the first instance proportional to the hydrogen ion concentration, though there are often secondary effects due to the other ions, and in all probability to undissociated molecules. Similar results have been obtained with seedlings by Cameron and Breazeale.†

Fernbach‡ and others have made systematic investigations of the effect of acids on enzyme actions. Fernbach gives a table containing the amounts of different acids just sufficient to inhibit the action of invertase on sugar, and from his numbers, and the dissociation constants of the respective acids given by Ostwald, I have calculated the hydrogen ion concentrations of the solutions in question; the results are given below:—

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* Kahlenberg and Austin, 'Journ. phys. Chem.,' vol. 4, p. 553 (1900); Kahlenberg and Mehl, *loc. cit.*, vol. 5, p. 113 (1901).

† 'Journ. phys. Chem.,' vol. 8, p. 1 (1904).

‡ Thèse, Paris, 1890, quoted by Effront, 'Enzymes,' English Edit., 1902, p. 69, *et seq.*

Table III.

Acids.	Inhibiting quantity.	Hydrogen ion concentration.
Sulphuric acid......	1/245 normal solution.	1/245 normal.
Tartaric „	1/75 „	1/280 „
Oxalic „	1/630 „	1/1000 „
Succinic „	1/30 „	1/700 „
Lactic „	1/9 „	1/265 „
Acetic „	5/6 „	1/266 „

It is clear that in this case, also, the retarding effect is, in the first instance, proportional to the chemical activity of the acid, though oxalic and succinic acids have a greater toxic action than would be expected.

Effect of Alkali upon the Reaction.

The influence of sodium hydroxide upon the reaction has been determined. It has been found that the velocity is not very appreciably influenced by solutions weaker than 1/2000 normal, but that in stronger solutions a retardation of the velocity is brought about. The retardation, unlike that caused by acids, depends upon the period of incubation, but the change is not a permanent one, since on neutralisation the original velocity is regained. Details are given in my former paper.*

Effect of Neutral Salts.

Numerous investigations of the influence of neutral salts on enzyme action have been carried out, but little of a general character can be deduced from the results. Dilute solutions have often a slightly accelerating action, which passes into a retardation in more concentrated solutions.

I have investigated the influence of halogens of the alkalis and alkaline earths, of the alkali sulphates, and of sodium acetate and carbonate. Only the halogen compounds exert a considerable retardation; the effects due to the others seem to be more of a secondary nature.

Some typical results are given below :—

Table IV.

	Constants.		Constants.
Lithium chloride, *m*/400	0·0059	Ammonium bromide, *m*/2000..	0·0136
Sodium chloride, *m*/400	0·0055	Barium chloride, *m*/200	0·0052
„ „ *m*/800.....	0·0093	„ „ *m*/400	0·0080
Potassium chloride, *m*/400 ..	0·0057	Strontium chloride, *m*/200....	0·0056
„ „ *m*/800 ..	0·0095	„ „ *m*/400....	0·0090
Ammonium chloride, *m*/400..	0·0058	Calcium chloride, *m*/200......	0·0051
„ „ *m*/800..	0·0094	„ „ *m*/400......	0·0084
Potassium bromide, *m*/800 ..	0·0075	Sodium fluoride, *m*/400	0·0170
„ „ *m*/2000..	0·0128	„ „ *m*/800	0·0246
Ammonium bromide, *m*/800..	0·0074	Control experiment	0·0280

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* Senter, *loc. cit.*, p. 301.

Owing to the direct oxidising action of H_2O_2 upon the iodides, it has been found impossible to complete the series by making measurements with corresponding solutions of these compounds. This point will be again referred to under the experiments dealing with iodine.

From the results given above it is evident that the retarding effect due to the halogen compounds is due to the halogen ion alone, since it is quite independent of the other ion present. It may be mentioned in this connection that according to Bredig* the catalysis of hydrogen peroxide by colloidal platinum is retarded by KCl and NH_4Cl, though not appreciably so by other neutral salts.

The results with sodium fluoride are particularly interesting, since it has long been regarded as a poison for micro-organisms, but without effect on enzymes.† According to Pavy,‡ however, it has a slightly deleterious action on enzymes, and this is quite borne out by the results given above.

Alkali Sulphates.—Experiments were carried out with potassium, sodium, and ammonium sulphates, in concentrations varying from *m*/50 to *m*/400. The results are as follows :—

Table V.

Salt used.	Constants.	Salt used.	Constants.
K_2SO_4, *m*/50	0·0265	Na_2SO_4, *m*/50	0·0360
„ *m*/200	0·0235	„ *m*/200	0·0308
„ *m*/400	0·0245	„ *m*/400	0·0288
$(NH_4)_2SO_4$, *m*/50	0·0280	Control experiment; no salt present	0·0288
„ *m*/200	0·0250		
„ *m*/400	0·0260		

From the results given it is evident that, while K_2SO_4 and $(NH_4)_2SO_4$ exert a slight retarding action, Na_2SO_4 in *m*/50 solution has a considerable accelerating effect, which practically disappears in *m*/400 solution. As having a possible connection with this result it may be recalled that, of the three sulphates, only the sodium salt crystallises with water (10 molecules).

Sodium Acetate and Sodium Carbonate.—The results are as follows :—

Table VI.

Salt used.	Constants.	Salt used.	Constants.
Sodium acetate, *m*/100	0·0272	Sodium acetate, *m*/1000	0·0345
„ „ *m*/200	0·0270	„ „ *m*/2000	0·0340
„ „ *m*/400	0·0250	Control experiment	0·0280
Control experiment	0·0180		

Salt used.	Constants.
Sodium carbonate, *m*/40	0·0070
„ „ *m*/80	0·0135
„ „ *m*/200	0·0194
Control experiment	0·0180

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* Bredig, 'Anorg. Fermente,' p. 84.

† Oppenheimer, *loc. cit.*, p. 41.

‡ Pavy, 'Journ. of Physiology,' vol. 22, p. 391 (1898).

Quite an appreciable acceleration is caused by sodium acetate, and its amount seems, curiously enough, to be almost independent of the salt concentration. It has been found that neither sodium acetate nor sodium sulphate appreciably catalyse hydrogen peroxide in the concentrations employed.

Effect of Alkali Salts with Oxidising Properties.

In my former paper,[*] experiments with $KClO_3$ and KNO_3 are described, and it was shown that these salts at 0°, even in 1/80,000 molar solution, exert a powerful depressing effect on the action, the constants at the same time decreasing as if the enzyme were being gradually oxidised. There seems, however, to be a depressing effect independent of the oxidation since, with the weaker solutions, there is a considerable decrease in the velocity, though the constants do not appreciably decrease during the action. This is also evident from the experiment with nitric acid quoted on p. 204.

Experiments have now been carried out with potassium perchlorate and potassium persulphate, an experiment with $KClO_3$ being made at the same time for the sake of comparison.

Table VII.

Salt used.	Constants.	Salt used.	Constants.
$KClO_4$, *m*/50,000	0·0039	KSO_4, *m*/200	0·0076
„ *m*/100,000	0·0070	„ *m*/400	0·0137
„ *m*/250,000	0·0133	Control experiment	0·0300
$KClO_3$, *m*/1,000,000	0·0054—0·0024		

It is interesting to note that the constants do not decrease during the action with potassium perchlorate and potassium persulphate, so that the enzyme is not being appreciably oxidised; there is, on the other hand, a marked decrease with potassium chlorate, from 0·0054—0·0024 in the course of 3 hours.

The results with potassium chlorate are interesting since this salt is a blood-poison, owing to its power of converting hæmoglobin into methæmoglobin. According to preliminary experiments by Professors Kobert and Schär,[†] potassium chlorate does not greatly retard the catalysis of hydrogen peroxide by blood; that this view is erroneous is evident from the results here given.

Potassium chlorate is not very poisonous towards the lower organisms.[‡]

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[*] Senter, *loc. cit.*, p. 304.

[†] Quoted by Bredig, *loc. cit.*, pp. 81 and 85

[‡] Loew, 'Die Giftwirkungen,' p. 17.

Effect of some Reducing Agents on the Reaction.

Measurements have been made with phenylhydrazine acetate, hydroxylamine hydrochloride, sulphuretted hydrogen, and formaldehyde, the results with the two former being interesting from their known property of combining with aldehyde and ketone groups.

Sulphuretted Hydrogen.—This body proved to be quite remarkably poisonous to the action, a solution containing 1/2,500,000 gramme-mol. reducing the rate to a half. The poisonous effect also depends greatly upon the period of incubation, the longer the incubation the greater the retardation. The constants also increase considerably during the action; this phenomenon is very likely due to the gradual oxidation of the H_2S by the H_2O_2.

The numerical results are appended:—

Table VIII.

Substance used and concentration.			Time of incubation.	Constants.
Sulphuretted hydrogen,		*m*/500,000	10 mins.	0·0062—0·0085
,,	,,	*m*/500,000	90 ,,	0·0018—0·0075
,,	,,	*m*/1,000,000	10 ,,	0·0073—0·0080
,,	,,	*m*/1,000,000	90 ,,	0·0025—0·0080
,,	,,	*m*/2,500,000	10 ,,	0·0076—0·0100
,,	,,	*m*/2,500,000	90 ,,	0·0054—0·0098
Without sulphuretted hydrogen			—	0·0190

It was observed by Faraday that platinum no longer brought about combination in detonating gas containing a little H_2S, and Bredig has shown that this gas is remarkably poisonous to the catalysis of H_2O_2 by colloidal platinum.*

Sulphuretted hydrogen has a slightly poisonous action on the lower organisms, but is a very energetic blood-poison, probably acting on the hæmoglobin, which it changes into a compound containing sulphur.†

Hydroxylamine.—This body has a considerably retarding effect, the constants decreasing slightly during the action.

Table IX.

Salt used.			Constants.
Hydroxylamine hydrochloride,		*n*/20,000	0·0008—0·0005
,,	,,	*n*/40,000	0·0047—0·0041
Without hydroxylamine			0·0180

Part of the hydrochloric acid remains uncombined and exerts a retarding action, but this is very small in so dilute a solution, and nearly the whole retardation is due to the hydroxylamine.

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* Bredig, *loc. cit.*, p. 65.

† Loew, *loc. cit.*, p. 56.

Phenylhydrazine acetate does not retard the action quite so strongly as hydroxylamine; the constants decrease considerably during the action:—

Table X.

Substance used.	Constants.
Phenylhydrazine acetate, *m*/5,000	0·0040—0·0010
„ „ *m*/10,000	0·0061—0·0025
„ „ *m*/20,000	0·0093—0·0041

As in the former case, the free acid present retards the action, but only to a small extent.

Both hydroxylamine and phenylhydrazine are exceedingly poisonous to the lower organisms, much less so to the higher animals.* They both retard the catalysis of hydrogen peroxide by platinum to a considerable extent.† Very few observations of their effect on enzymes have been made.

Formaldehyde.—As is well known, this substance is very poisonous for the lower organisms, and is now largely used as an antiseptic.

According to Effront,‡ very minute amounts slow down the hydrolysis of starch by diastase, on the other hand, it has little influence on the activity of rennet.§ From the results given it is clear that formaldehyde only slightly affects the activity of hæmase:—

Table XI.

	Constants.
Formaldehyde, *m*/1000	0·0300
„ *m*/2000	0·0337
Without formaldehyde	0·0372

It may be mentioned that hydrogen peroxide does not appreciably oxidise formaldehyde in the dilution used in these experiments.

Effect of Mercuric Salts on the Reaction.

Experiments have been carried out with mercuric chloride, bromide, and cyanide. The two former have an exceedingly toxic effect, while the latter has very little action:—

Table XII.

Salt used.	Constants.	Salt used.	Constants.
$HgCl_2$, *m*/250,000	0·0020—0·0004	$HgBr_2$, *m*/80,000	0·0040—0·0009
„ *m*/500,000	0·0033—0·0006	„ *m*/200,000	0·0078—0·0032
„ *m*/1,000,000	0·0052—0·0018	$Hg(CN)_2$, *m*/400	0·0154
„ *m*/2,000,000	0·0098—0·0054	„ *m*/800	0·0218
$HgBr_2$, *m*/40,000	0·0025—0·0013		
Control experiment without mercuric salt			0·0250

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* Loew, *loc. cit.*, pp. 89, *et seq.*

† Bredig, *loc. cit.*, p. 76.

‡ Effront, 'Enzymes,' p. 117.

§ Oppenheimer, *loc. cit.*, p. 114.

Mercuric salts are energetic poisons for both higher and lower organisms.[*] Paul and Krönig[†] have shown that the poisonous action on bacteria diminishes from the chloride through the bromide to the cyanide, and it is known that the electrolytic dissociation decreases in the same order.

Mercuric chloride in the amount of one-millionth paralyses the action of diastase on starch[‡] and, according to Bredig,[§] is a very active poison for the platinum catalysis of hydrogen peroxide.

From the quantitative measurements given above it is clear that mercuric chloride is about five times as toxic as mercuric bromide towards the hæmase catalysis,[‖] and at least 20,000 times as toxic as mercuric cyanide.

Effect of some other Poisons on the Reaction.

Carbon monoxide.—As is well known, carbon monoxide is very poisonous towards the higher animals on account of its property of forming a stable compound with the hæmoglobin of the blood. It was therefore a matter of interest to investigate its effect on the enzyme-catalysis of hydrogen peroxide, since the enzyme used is got from blood.

In order to get as much of the gas as possible dissolved, measurements were carried out at 0°; the gas was passed through a dilute solution of the enzyme in a bottle for 4 minutes, then, without stopping the current, the hydrogen peroxide was added and the stopper inserted, the bottle being thus filled with an atmosphere of the gas.

It was found that the gas exerted no appreciable poisoning effect; the constant in the presence of CO was 0·0085, and in its absence 0·0090, an agreement with the limit of experimental error.

Carbon monoxide is not poisonous towards the germination of seeds,[¶] nor towards bacteria;[¶] according to Buchner,[**] it does not affect the fermentation of sugar by zymase. It retards the catalysis of hydrogen peroxide by colloidal platinum.[††]

Iodine.—Iodine, as well as bromine and chlorine, are poisonous for all living matter,[‡‡] and Bredig,[§§] in his interesting experiments on the platinum catalysis of hydrogen peroxide, found that the first-mentioned substance, even in a dilution of 1 gramme-mol. in 7,000,000 litres, reduces the rate of reaction to half its original value.

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[*] Loew, 'Die Giftwirkungen,' p. 85.

[†] 'Zeit. f. physik. Chemie,' vol. 21, p. 414 (1896).

[‡] Effront, *loc. cit.*, p. 116.

[§] Bredig, *loc. cit.*, p. 81.

[‖] Up to the present the extent to which solutions of mercuric bromide are hydrolysed is not known, so that the relative ion concentrations of these solutions cannot be calculated, *vide* Luther, 'Zeit. phys. Chem.,' vol. 47, p. 107 (1904).

[¶] Loew, *loc. cit.*, p. 108.

[**] See Ikeda, 'Zeit. physik. Chemie,' vol. 37, p. 26 (1901).

[††] Bredig, *loc. cit.*, p. 78.

[‡‡] Loew, *loc. cit.*, p. 16.

[§§] Bredig, *loc. cit.*, p. 74

I have used in my experiments iodine dissolved in water and also in aqueous solution of potassium iodide. The results are :—

Table XIII.

Substance used.	Constants.
Iodine dissolved in water, *m*/4000	0·0116—0·0160
,, ,, ,, *m*/8000	0·0168—0·0190
Iodine, *m*/40,000, potassium iodide, *m*/10,000 ...	0·0070
Control experiment without iodine	0·0185

The interesting result is thus obtained that an aqueous solution of iodine exerts only a very slight poisonous action on the enzyme, while a solution in potassium iodide, which contains the iodine in the form of I_3 ions, is distinctly poisonous, though very far behind what Bredig found for the platinum catalysis. Experiments carried out with potassium iodide in 1/10,000 molar solution show that the poisonous effect does not depend upon its presence, since the action was, if anything, accelerated under these conditions. It was observed, however, that the colour of the iodine solution partly disappeared on treatment with H_2O_2, so that some chemical change had evidently taken place.

Arsenious Oxide.—This body is a deadly poison for higher and lower organisms,* but has been found by various investigators to have only a slightly poisonous effect upon enzymes.† This is fully confirmed by the results here given :—

Table XIV.

Substance used.	Constants.
As_2O_3, *m*/2000............	0·0224
,, *m*/4000............	0·0213
Without As_2O_3	0·0214

From the total number of cubic centimetres of permanganate used, the amount used up by the As_2O_3 was subtracted.

The oxidation of the As_2O_3 by hydrogen peroxide is very slow in the dilution here employed, and it was found that this oxidation is not in the least accelerated by the simultaneous decomposition of the hydrogen peroxide.

Discussion of the Results.

The Mechanism of the Catalysis by Hæmase.—Before discussing generally the results obtained with poisons, the mechanism of the catalysis of hydrogen peroxide by hæmase may be briefly considered. In this connection it must, in the first place, be taken into consideration that we are dealing with a heterogeneous reaction, since the hæmase is, in all probability, present in the solution in a colloidal state. According to our present views, such solutions form a two-phase system, the colloid being suspended in the liquid in a very fine state of division.

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* Loew, *loc. cit.*, p. 19.

† Kobert, *loc. cit.*, p. 153, Buchner, 'Berichte,' vol. 31, p. 2675.

It has recently been insisted upon, more particularly by Nernst,* that we are not entitled to apply the equations governing reaction velocity in homogeneous systems to heterogeneous systems.

According to Nernst there is always equilibrium at the boundary surface between two phases, and the changes which take time are (1) chemical actions in the two phases, and (2) diffusion of substances to and from the boundary. Examples of the first type, in which the reaction velocity in one of the two phases is slow compared with the rate of diffusion, are given in the paper quoted; reactions of the second type, in which the velocity of diffusion determines the rate of action, have been experimentally investigated by Brunner.†

It may be taken as proved that the rate of solution of marble in acids is conditioned by a diffusion process, and the same is true of the rate of combination of hydrogen and oxygen in contact with a platinum surface. One criterion for the dependence of a reaction velocity upon diffusion is the effect produced by stirring the solution—this shortens the diffusion path, and thus increases the speed of reaction.

Nernst‡ is also of opinion that the same explanation holds for the decomposition of hydrogen peroxide by colloidal platinum—that the actual decomposition is very rapid compared with the diffusion of the peroxide to the surface of the catalysor.

We will now inquire whether the catalysis of hydrogen peroxide by hæmase can be represented in a similar way. Since the particles of a colloidal solution are in a continual state of motion, we may assume that stirring would not appreciably affect the reaction velocity. We may imagine that each particle of colloid has adhering to it a layer of liquid; that the rate of decomposition of the peroxide by the enzyme is very great, and that the concentration outside the adhering layer is kept constant by the motion of the colloidal particles. The rate of decomposition of the peroxide would then be determined by the rate of its diffusion through the adhering film, and, since the rate of diffusion is proportional to the difference of concentration on the two sides of the film, a simple explanation would be given of the observed fact that the reaction velocity is proportional to the concentration of the peroxide. Some support is given to this view by the fact that the temperature coefficient of the hæmase catalysis for 10° is 1·5, which agrees with that found by Brunner for the velocity of solution of benzoic acid in water, but is much smaller than the average for reactions in a homogeneous system.*

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* Nernst, 'Zeit. physik. Chemie,' vol. 47, p. 52 (1904).

† Brunner, 'Zeit. physik. Chemie,' vol. 47, p. 56 (1904).

‡ *Loc. cit.*

I have previously shown that while the reaction velocity in very dilute solutions is proportional to the hydrogen-peroxide concentration, in stronger solutions deviations occur,† which can be summed up by saying that the reaction proceeds more rapidly in the relatively more dilute peroxide solutions. On the diffusion hypothesis this can be simply explained on the assumption that the diffusion process is more disturbed in strong solutions by the oxygen given off from the surface of the particles.

While the above hypothesis affords a simple explanation of all the facts in the hæmase catalysis, it by no means follows that it can be extended to enzyme actions in general. The assumption made is that the reaction at the surface is much quicker than the diffusion changes concerned, and, while this is so in the dissolving of magnesia by acids, and, in all probability, in the catalysis of hydrogen peroxide by hæmase and by platinum, it may not be so in reactions between enzymes and more complicated substances.‡

As regards the catalysis itself, it may be said with certainty that it is not due to the large surface area of the colloid particles acting mechanically on the peroxide, since many colloidal solutions have no catalytic effect whatever. It may be due to the formation of a chemical compound between the peroxide and the enzyme, which, being unstable, breaks down into water, oxygen, and the enzyme, or the compound may enter into double decomposition with another molecule of the peroxide.§ Two observations which I have made may contribute something to the elucidation of these changes. As mentioned on p. 212 oxidations are not accelerated during the catalysis, so that apparently no strongly oxidising intermediate peroxides are formed,* nor is "active" oxygen evolved. It was also found that the action has exactly the same initial velocity whether the solutions be carefully freed from dissolved oxygen by a current of hydrogen, or whether, as usual, a little of the former gas be present.

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* van't Hoff, 'Vorlesungen,' vol. 1, p. 225.

† Senter, *loc. cit.*, p. 286.

‡ Since this paper was written my attention has been drawn to a paper by Herzog ('Zeit. für physiolog. Chemie,' vol. 41, p. 416 (1904).), in which the attempt is made to apply Nernst's diffusion hypothesis to all enzyme actions. Without further investigation it is impossible to pronounce a definite opinion on the matter, and Herzog's re-calculations of Henri's results scarcely serve to prove the truth of his premises. Having regard to the results of Henri ('Lois Générales de l'Action des Diastases,' Paris, 1903), A. J. Brown ('Journ. Chem. Soc.,' vol. 81, p. 393, 1902), and others, and to the temperature coefficient of enzyme actions as determined by O'Sullivan and Tompson ('Journ. Chem. Soc.,' vol. 59, Part I, p. 834 (1890)), and Müller-Thurgan ('Thiels Wirtschaftliche Jahrbuch,' 1885, p. 795), it seems not unlikely that the relative parts played by diffusion and by the actual chemical change in determining the reaction velocity depend upon the conditions of experiment.

§ Compare Kastle and Loevenhart, 'Am. Ch. J.,' vol. 29, pp. 397 and 563 (1903).

The Action of Poisons.—The question as to the mechanism of the action of "poisons" on the hæmase catalysis of hydrogen peroxide may now be considered. If the enzyme exists as a colloid in solution several explanations† seem possible:—

(*a*) Part of the enzyme may be rendered inactive by forming a chemical compound with the poison.

(*b*) Part of the surface of the particles may become covered with a thin layer of the poison or one of its decomposition products, thus preventing further action on the peroxide.

(*c*) The relation of the particles to the surrounding medium may be altered in various ways (change of surface tension, alteration of relative difference of potential, &c.) through addition of a poison.

Doubtless other explanations may be suggested. It is also exceedingly probable that all poisons do not act in the same way.

In this connection it may be noted that, according to Kastle and Loevenhart, the retarding effect of poisons on the catalysis of H_2O_2 by metals and other inorganic catalysors is due in most cases to formation of an insoluble film (compound between poison and catalysor) on the surface of the catalysor.

The action of acids and alkalies on the hæmase catalysis is of particular interest, since it has been shown, more especially by Hardy,‡ that minute traces of these bodies affect profoundly the relation between the colloidal particles and the surrounding medium. According to Linder and Picton,§ Hardy,‖ and others, the effect of acids in precipitating colloids is proportional to their electrical conductivity, *i.e.*, to the hydrogen ion concentration, but this is probably not connected with the similar effect on the hæmase catalysis because the former action is irreversible, whereas I have shown that the latter is reversible. It cannot be said that any very satisfactory explanation of the effect of acids, alkalies, and other electrolytes on colloids has yet been given.‖

With regard to the reaction under consideration I am inclined, in most cases, to favour a chemical explanation of the toxic effect. Acids, for example, may form with the enzyme compounds which are inactive towards hydrogen peroxide. If the affinity between hæmase and the acid is small, in other words, if the enzyme acts as a weak base, the amount combined, and consequently the retardation will be proportional to the strength of the acid. We have already seen that hæmase and most other enzymes are rendered inactive by small quantities of alkali, and that they regain their activity on the solution being neutralised. These facts seem to lend some support to a suggestion I have already made on a former occasion,* that at least some enzymes belong to the class of amphoteric substances which are, under ordinary circumstances, neutral, but in the presence of bases develop acid properties and can combine with acids to form salts. Within the last few years it has been shown that many albuminous substances are amphoteric.

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* Or, if formed, their velocity of decomposition, either of themselves or in contact with hydrogen peroxide, is much greater than the reaction velocity between them and such a reducing substance as arsenious oxide.

† Compare Bredig, *loc. cit.*, p. 86.

‡ 'Roy. Soc. Proc.,' vol. 66, p. 110 (1899—1900).

§ Linder and Picton, 'Journ. Chem. Soc.,' vol. 67, p. 66 (1895).

‖ *Vide* Hardy, *loc. cit.*, p. 124; Bredig, *loc. cit.*, pp. 9—22; Freundlich, 'Zeit. phys. Chemie,' vol. 44, p. 129 (1903).

The slight retardation caused by most neutral alkali salts is due, in all probability, to increased viscosity of the solution. This cannot apply, however, to the considerable toxic effect of the chlorine and bromine ions and, since a similar retardation of the platinum catalysis has been observed, it may be due to some action between the hydrogen peroxide and halogen salts. Kastle and Loevenhart† regard the retardation of the platinum catalysis as due to the formation of surface films of the insoluble platinous halides.

The retarding influence exerted on the action by oxidising agents is very remarkable. It is not due to oxidation of the enzyme in most cases, as is clear from the fact that the constants do not decrease during the action in presence of potassium perchlorate and nitric acid. On the other hand, potassium chlorate in exceedingly dilute solution seems to oxidise the enzyme, and since the neutral salt itself has very weak oxidising properties, its activity in this case must be due to the presence of the peroxide. That it is due to chloric acid set free by the hydrogen peroxide, acting as an acid, is scarcely likely, since the acidic properties of the latter are very weak. In this connection it is interesting to note that potassium persulphate has very little effect on the action, whereas persulphuric acid has a high oxidation potential.

The great retardation caused by some reducing agents, such as sulphuretted hydrogen and hydroxylamine, is also rather difficult to account for. Bredig‡ suggests that the poisonous effect of the former on the platinum catalysis is due to the deposition of sulphur on the surface of the platinum, whereas Kastle and Loevenhart regard it as being due to formation of a surface film of platinum sulphide. Neither of these explanations seems to apply to the effect on the hæmase catalysis, since I have observed that the constants increase considerably during the action (p. 209). It seems much more probable that the H_2S renders the enzyme inactive, perhaps by forming a loose compound with it, and that the gradual increase of the constants is due to recovery of the enzyme owing to oxidation of the poison. The toxic action of mercuric salts, and of hydrocyanic acid, seems most simply explicable on the theory of formation of loose compounds between them and the enzyme.

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* *Loc. cit.*, p. 301.

† *Loc. cit.*

‡ *Loc. cit.*, p. 87.

Summary of Results.

1. Quantitative measurements have been made of the effect of various substances on the rate of decomposition of hydrogen peroxide by hæmase, an enzyme obtained from blood.

2. The probable mechanism of the catalysis in question has been discussed, and reasons have been given for supposing that what is actually measured is the rate of diffusion of hydrogen peroxide to the enzyme.

3. The ways in which "poisons" may exert their effect on the action have been discussed, and reasons have been given for preferring, in some cases, a chemical explanation of the observed facts.

4. From the results obtained with acids and alkalis, as well as from the results of other observers, it has been concluded that at least some enzymes are amphoteric substances, *i.e.*, substances which are neutral in aqueous solution but can combine both with acids and with bases to form salts.

I have much pleasure in thanking Dr. Charles A. Kohn for the facilities he has kindly allowed me for carrying on my work.

"On certain Properties of the Alloys of Silver and Cadmium."

By T. KIRKE ROSE, D.Sc. Communicated by C. T. HEYCOCK, F.R.S. Received February 9,—Read February 11, 1904.

[PLATE 10.]

It has long been known that an alloy of silver and copper is not a satisfactory material for the trial plates which are used in testing the fineness of the Imperial silver coin and of silver wares before they are hall-marked. As long ago as the year 1580 the lack of homogeneity of silver-copper alloys was well known to the German metallurgists,[*] and in 1852 Levol concluded[†] that the only uniform alloy of the series contained 718·93 parts of silver and 281·07 parts of copper, a composition which corresponds to the formula Ag_3Cu_2. In 1875 Roberts-Austen, as the result of very carefully conducted experiments,[‡] found that under the most favourable circumstances the difference in composition between the centre and corners of a small ingot amounted to 1·2 parts per 1000, and was generally much greater. In 1899 when further attempts were made to prepare ingots of silver and copper of uniform composition,[§] similar results were obtained, although many castings were made in accordance with the method recommended by E. Matthey.[||]

A consideration of the cooling curve of the standard silver-copper alloy, containing silver 92·5, copper 7·5 by weight, which was obtained by Roberts-Austen,[¶] and is reproduced in C fig. 1, shows that such segregation must necessarily take place. The initial freezing point d_1 of this alloy, in which the percentage by atoms is silver 87·9, copper 12·1, is at about 900°. At this temperature a solid solution rich in silver begins to crystallise out, but solidification is not complete until the temperature has fallen to 778° (d_2 fig. 1), when the mother liquor contains only 60 atoms of silver to 40 of copper, that is to say, the proportion found by Heycock and Neville to be present in the eutectic alloy.[**] During the pasty stage ample time is allowed for the segregation of the silver-rich constituent, with the result that the distribution of silver in the solidified metal is not uniform. The amount of segregation varies with the dimensions of the ingot, the shape and temperature of the mould in which it is cast, the temperature of casting, and the rate of cooling. In the case of ingots weighing about 125 ozs. troy (4 kilos.), the ordinary weight of the Imperial trial plates, the centre of the mass is usually richer in silver than the outside to the extent of from 1—3 parts per 1000.

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[*] See pp. 20 and 26 of 'Allerfurnemisten Mineralischen Eerzt und Bergwerksarten,' by L. Ercker. Published at Frankfort in 1580.

[†] 'Ann. de Chimie et de Phys.' (3), vol. 36 (1852), p. 193 and vol. 39 (1853), p. 163.

[‡] 'Roy. Soc. Proc.,' vol. 23 (1875), p. 481.

[§] Thirtieth Annual Report of the Mint (1899), p. 69.

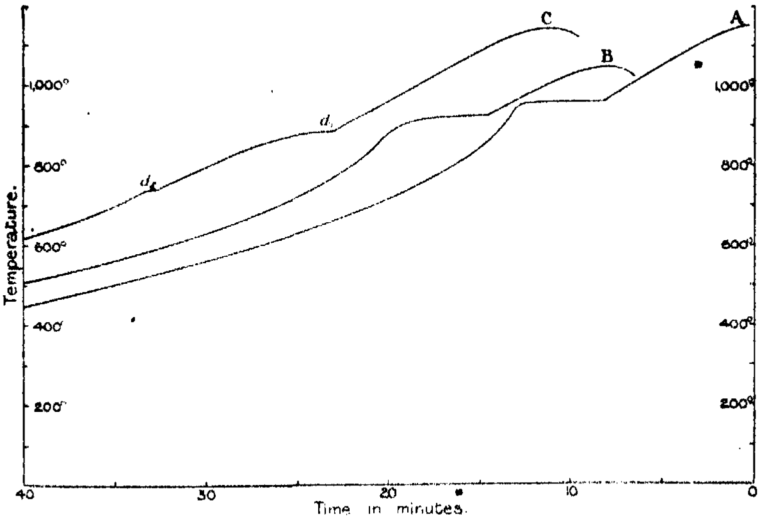
[||] 'Roy. Soc. Proc.,' vol. 55 (1894), p. 265.

[¶] First Report to the Alloys Research Committee, 'Inst. Mech. Eng. Proc.,' 1891, p. 543.

[**] 'Phil. Trans.,' A, vol. 189 (1897), p. 25.

When a pure metal such as silver is solidified (Curve A, fig. 1) no pasty stage occurs. The part first solidified is of the same composition as that still remaining liquid, and the temperature remains constant until the whole is solid.

FIG. 1.



The solidification of an alloy containing 91·66 per cent. of gold and 8·33 per cent. of silver shows similar characteristics,* and remains uniform in composition under all conditions. Having regard to these considerations and to the experience that has been gained of the difficulties attending the preparation of a homogeneous standard silver trial-plate, it seemed more likely that such a plate would be successfully prepared by using a different alloy than by making fresh experiments with silver and copper. The first alloy to be tried consisted of silver 925 parts, gold 75 parts, but although the plates prepared were, doubtless, uniform in composition, the difficulties connected with the assay of the plates were insuperable. It is obvious that the fineness of the plate could not be compared with that of silver coin by the cupellation process, for the reason that the gold would not be separated from the silver in that case. Nor were the wet processes of assay, which involve dissolution in nitric acid, found to be much more convenient. When the alloy was digested with nitric acid in the ordinary way, at a moderate temperature, large and variable quantities of silver were retained by the gold. When the alloy was boiled in moderately strong nitric acid for 30 minutes, the gold still retained about 0·2 per 1000 of the silver, and a further variable amount was carried off by the vapour rising from the boiling liquid and lost.

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* 'Roy. Soc. Proc.,' vol. 71 (1903), p. 161.

It was, therefore, necessary to discover some other alloy which would be at once uniform in composition and easy to use as a standard of comparison.

An examination of the cooling curves of a number of alloys containing 92·5 per cent. of silver afforded evidence that the silver-cadmium alloy would prove to be the most suitable one for trial-plates. Unlike the alloys containing gold, tin, or antimony, the cadmium alloy presents no difficulty in connection with the assay by the ordinary methods, and the cooling curve, B fig. 1, bears a close resemblance to that of a pure metal, the fall in temperature during solidification not being great. The completion of solidification, however, is marked by a slight momentary change of direction of the curve, pointing to the freezing of a small quantity of material of the nature of an eutectic alloy, and it seemed possible that this might correspond to a change in the distribution of the silver throughout the mass, resulting in a lack of homogeneity.

In order to test this, ingots of silver and cadmium of standard fineness were prepared and rolled out. Some difficulties were at first encountered in the melting of the alloy. If pieces of solid cadmium, even when warmed, are added to molten silver, the action is very violent, and varying losses of cadmium by oxidation and volatilisation take place, so that the resulting alloy is seldom of the exact composition required. The method eventually adopted consists in pouring molten silver, heated only slightly above its melting point, into a large crucible containing melted cadmium at a black heat and covered with charcoal. The crucible is then placed in the fire, raised to a bright red heat as quickly as possible, and the alloy well stirred and poured into a closed mould. Under these conditions, when operating with 4 or 5 kilos. of material, the mixing of the metals takes place with comparative quietness, and the loss of cadmium is reduced to about 0·15 per cent. by weight of the alloy. In order to prepare a standard trial-plate, which consists of 925 parts of silver and 75 parts of base metal, it is accordingly necessary to melt 76·5 parts of cadmium and to add 925 parts of silver to it. A large part of the loss appears to take place on the addition of the silver to the cadmium, dense fumes of oxide of cadmium being given off, but on merely melting and re-casting a standard ingot of 5 kilos., the proportion of silver present rises from 92·50 per cent. to about 92·58 per cent.

The silver-cadmium standard alloy is more ductile and is whiter than the corresponding alloy of silver and copper, which has a slightly yellowish tinge. The ingots obtained were 21·5 cm. long, 15·3 cm. wide and 1·25 cm. thick. They were rolled to a gauge of 1·25 mm. and pieces cut from all parts were assayed, with the results that the plates* were found to be practically of uniform composition. The cadmium does not interfere with the ordinary methods of assay, no difference in results due to interference being observable when the trial-plates were compared with pure silver by the Gay-Lussac and Volhard processes of assay. In practice when the fineness of a silver-copper alloy is being compared with that of the trial-plate, by means of the Volhard process, the nitric acid solution of the copper alloy would be coloured blue, while that of the cadmium alloy would remain colourless. This would interfere with the correctness of the comparative final readings, but in order to avoid this difficulty, it is sufficient to add a piece of copper of the appropriate weight to the solution of the cadmium alloy. When the silver-cadmium alloy is cupelled, the cadmium burns off and the loss of silver is about four parts in 10,000 more than if the alloying metal were copper. In comparisons by the cupellation process, it is, therefore, essential that the assay pieces should be made of similar composition by suitable additions of base metals. This course presents no difficulty and in no way detracts from the value of the trial.

The results of these experiments show that trustworthy and convenient trial-plates can be made of silver and cadmium, but it remained to be determined by further study of the properties of the series of alloys whether the uniformity in composition of the trial-plates was fortuitous, or whether it was the inevitable result of its constitution.

The silver-cadmium series has been investigated by Gautier,† who stated that the freezing-point curve consisted of two parts meeting at a point corresponding to the alloy containing about 42 per cent. of silver and that the alloys appeared to consist of isomorphous mixtures of a compound of silver and cadmium with one or other of the pure metals. In order to confirm these observations of Gautier a number of alloys, consisting of silver and cadmium, were prepared and analysed. The silver used for this purpose was purified with the precautions adopted in the preparation of fine "proof" silver in the Mint and was 1000 fine. The cadmium was purchased as pure and was examined for impurities, but none were detected. The proportion of silver in the alloys was determined by the Volhard process of assay. Cooling curves were taken of the alloys by means of a Le Chatelier thermocouple and the recording pyrometer described by Roberts-Austen* and the following results were obtained :—

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* One of the plates was sent to Mr. F. W. Harrold, the Assay Master at the Goldsmith's Hall, and another to Mr. H. Westwood, one of the Assay Masters of the Assay Office, Birmingham. They have kindly made a number of assays on the plates, and state that the composition of each plate is uniform.

† 'Bull. de la Soc. d'Encouragement,' Fifth Series, I, p. 1315 (1896).

Freezing-points of the Silver-Cadmium Alloys.

Percentage of silver by weight.	Atomic percentage of silver.		Freezing-points.	
100·0	100·0		961°·5	
95·01	95·18		956·5	(920°)
92·63	92·87		948	(916)
92·57	92·81		945	(913)
88·80	89·16		918	(889)
87·20	87·60		907	(865)
84·59	85·07		895	(858)
83·34	83·84		893	(854)
79·94	80·50		854	
74·98	75·65		818	
66·10	66·80		810	
63·83	64·64		795	(718)
57·74	58·62		720	(695)
54·39	55·27		720	(424)
51·39	52·28		720	(430)
49·36	50·27		694	(419)
41·68	42·57		665	(619)
39·85	41·26		676	(643)
30·11	30·88	(590°)	571	
29·52	30·27	(586)	569	
21·12	21·74		446	(338)
9·12	9·42	(446)	332	
1·20	1·22		315	
0·60	0·61		320	
0·0	0·0		323	

The temperatures in brackets denote subsidiary freezing points which are generally below but sometimes above the main freezing points.

The curve of equilibrium between liquids and solids of the series is given in fig. 2. It has been plotted from the results given in the table. The upper continuous line is the liquidus curve. The solidus curve, which is not complete, is represented by the lower line, and is based on a study of the cooling curves, and of the micro-structure of chilled specimens.

When alloys containing more than 80 per cent. of silver† are allowed to cool at a moderate rate, the greater part of the mass solidifies at a definite temperature, leaving a very small part only to solidify at a lower temperature. The final freezing point is marked by a minute but distinct check in the rate of cooling. It becomes less marked as the percentage of silver falls below 95 per cent., and disappears altogether before the 80-per-cent. alloy is reached. The 80-per-cent. alloy itself solidifies nearly as a whole, and its cooling curve resembles that of a compound, or a pure metal. There is little doubt that ingots 800 fine in silver would be uniform in composition. As the percentage of silver falls from 80—65 per cent., the initial freezing or liquidus point becomes of less importance, and the pasty stage more pronounced and of longer duration.

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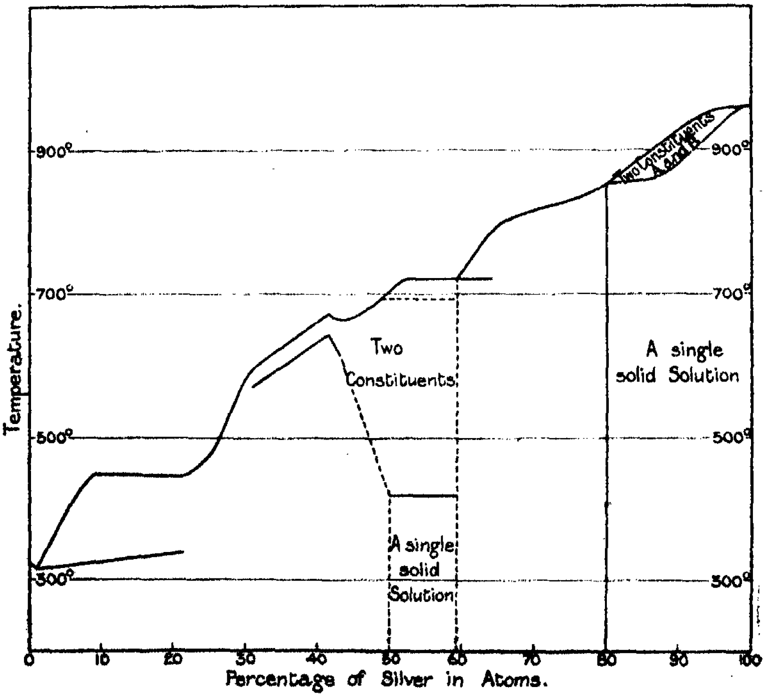
* 'Inst. Mech. Eng. Proc.,' Oct., 1891, p. 543.

† Both here and subsequently "per cent." is used for "number of atoms per cent." It happens, however, that this is nearly the same as the percentage by weight, the atomic weights of silver and cadmium differing but little.

Fig. 2.—Curves of Equilibrium of Silver and Cadmium.



The alloys containing about 66 per cent. of silver and approximating in composition to that required by the formula Ag_2Cd are somewhat less ductile than those members of the series which are richer in silver. They are more readily attacked by nitric acid than the alloys containing either more or less silver. This points to a lack of homogeneity, a conclusion that is supported by the shape of the cooling curve of the 64·64-per-cent. alloy. There is here a long pasty stage between the initial freezing point at 795°, and a second point at about 718°. During this range of temperature the slowness of the rate of cooling shows that solidification proceeds continuously and that the part of the mass remaining liquid undergoes a continuous change in composition. At the point when solidification is completed there is a more pronounced evolution of heat at about the same temperature as that at which solidification begins in the alloys containing from 52—58 per cent. of silver. The liquidus curve appears to show a small cusp corresponding to the compound Ag_2Cd, but it is probable that the compound Ag_2Cd, which was detected by Heycock and Neville in solution in other metals* is partly or entirely dissociated when melted by itself.

The alloy containing 58·62 per cent. of silver has two freezing points at 720° and 695°, separated by a pasty stage. The alloys containing from 52—55 per cent. of silver have freezing points at 720° and 420°. The eutectic solidifying at 695° was not observed in the cooling curves of these alloys, although there is little doubt that it must exist, particularly in view of the micro-structure. The 50-per-cent. alloy solidifies at 694°, and shows the eutectic point at 420°.

In the series containing from 50—60 per cent. of silver, the pasty stage succeeding the initial freezing point gradually diminishes as the percentage of silver is reduced, until in the 50-per-cent. alloy the fall of temperature during solidification is only about 20°, whereas in the 75-per-cent. it is nearly 100°. Nevertheless the freezing point of the 50-per-cent. alloy is not so sharp as that of an undissociated compound, and after the temperature has fallen at a normal rate to about 420° another considerable evolution of heat takes place, during which the temperature remains stationary. The point is also observable in the cooling of the 52-, 55-, and 58-per-cent. alloys, becoming successively smaller and dying away at about the 60-per-cent. alloy. Prolonged heating at various temperatures between 420° and 695° had not any apparent effect on the specimens, which retained their shape when not subjected to stress. When, however, a cast bar with composition corresponding to the formula AgCd was subjected to a bending stress equal to 10 grammes per square millimetre of cross section (about 14 lbs. per square inch), it was found to become suddenly plastic and to bend almost double without cracking at a temperature of 450°. When chilled at temperatures somewhat above 420° the specimens assumed a red or lilac tint, especially after light polishing, which is not so markedly observable in the specimens chilled from below 420°. The colour is observable in all the alloys containing from 40—50 per cent. of silver, and is always confined to the surface layer. The similar case of the silver-zinc alloy AgZn has been investigated by Heycock and Neville,* who also refer to the colour of the alloy AgCd.

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* "The Freezing-point of Triple Alloys," 'Chem. Soc. Trans.,' vol. 65 (1894) p. 65.

The cooling curves of some alloys containing about equal numbers of atoms of silver and zinc were also prepared for comparison, and were found to be very similar to the cooling curve of AgCd. The freezing point of the *alloy containing 51 atoms of zinc to 49 atoms of silver* is at 693°, and the evolution of heat by the alloy in the solid state is at 281°. The corresponding temperatures in the case of the alloy containing equal numbers of atoms of silver and zinc were found to be 690° and 271°. These results can be correlated with the facts observed by Heycock and Neville, who showed that the silver-zinc alloy could be made to assume a red tint if heated to a temperature near 300°, the lowest effective temperature being 285°, and suddenly chilled. The disappearance of the red tint thus appears to coincide with an evolution of heat in both cases. The red tint can also be obtained in either case by abrasion. It is well shown in filings and sometimes in polished specimens.

The liquidus curve of the silver-cadmium alloys shows a well-marked *cusp at about the 40-per-cent. alloy, pointing to the existence of the* compound Ag_2Cd_3. This alloy is hard and excessively brittle, breaking with a conchoidal fracture, a proof of homogeneity of structure.

The remainder of the freezing point curve is of an ordinary type, consisting of two branches meeting at a minimum at about the alloy containing 1·2 per cent. of silver, which solidifies at 315° or 8° below the freezing point of pure cadmium.† Further additions of silver raise the freezing point until a maximum of 676° is reached at the 40-per-cent. alloy. A branch of the curve of equilibrium was observed containing about 10 per cent. of silver solidifying at 332°.

The liquidus curve is thus seen to consist of 7 parts, which are as follows:—

(1) Between pure silver and the compound Ag_4Cd, convex upwards. The two constituents appear to be isomorphous.

(2) Between the compounds Ag_4Cd and Ag_2Cd, concave upwards.

(3) Between the compounds Ag_2Cd and Ag_3Cd_2. Nearly a straight line with a horizontal branch corresponding to the freezing point of the compound Ag_3Cd_2.

(4) Between the compounds Ag_3Cd_2 and AgCd, there is a horizontal branch corresponding to the freezing point of the compound Ag_3Cd_2. There is also probably another corresponding to the freezing point of the

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* 'Camb. Phil. Soc. Proc.,' vol. 9, Pt. 4, 1896.

† Rudberg ('Poggend. Annal.,' vol. 71, 1847, p. 460) and Riemsdijk ('Archives Néerlandaises,' vol. 3, 1868, p. 29) both gave the melting-point of cadmium as 320°, and *Gautier (loc. cit.) takes it as 322°. The temperature of 323° adopted here was* determined by comparison with the melting-point of pure lead, which was taken as 326°.

compound AgCd, and a third corresponding to the freezing point either of the compound $AgCd_3$ or of a eutectic alloy consisting chiefly of this compound.

(5) Between the compounds AgCd and Ag_2Cd_3. A curve concave upwards.

(6) Between the compounds Ag_2Cd_3 and $AgCd_3$.

(7) Between $AgCd_3$ and cadmium. A curve with a distinct minimum at about 1·2 per cent. of silver. There are two horizontal branches, one due to the solidification of a eutectic of this composition, and the other to the freezing of the compound $AgCd_3$.

Micro-structure of the Alloys.

The alloys containing upwards of 80 per cent of silver all present similar characteristics. Their structure is well developed on polished surfaces by dipping them for a few seconds in hot nitric acid of a specific gravity 1·25. Slowly cooled specimens, in which the solidification occupies about 5 minutes and the subsequent cooling to a low red heat about half an hour, are seen to consist of crystallites of a silver-rich body set in a darker coloured matrix which has been more deeply etched by the acid than the crystallites (see fig. 3, Plate 10). The limiting case of pure silver shows no matrix and the crystallites are large, the crystal grains in small specimens being from 5—8 mm. in diameter. Similarly no matrix was observed in the alloy containing 97·3 per cent. of silver but it was detected in the 95-per-cent. alloy, and showed some increase as the silver diminished to 80 per cent. At the same time the size of the crystallites diminished to a diameter of about 1 mm. When these alloys were re-heated for from 1—4 hours at temperatures intermediate between the initial freezing point and the "eutectic" point referred to above, the crystal grains broke up and a fine network of the dark-coloured matrix was formed. When reheated at any temperature above a red heat but below the final solidification point, the matrix disappeared and crystals were formed occupying the whole area of the field. The higher the temperature (below this point) and the longer the time during which it was maintained, the larger the crystals grew and the straighter and more regular became their bounding faces. All the specimens were chilled after re-heating.

It appears, therefore, that at all temperatures below the solidus curve, these alloys are homogeneous, consisting of a single solid solution, doubtless consisting of varying proportions of silver, and the compound Ag_4Cd the existence of which has been referred to by Heycock and Neville.* These two substances, silver and Ag_4Cd, must be regarded as isomorphous. It follows that the more slowly these alloys are cooled, the more uniform the composition should be. It should be possible to prepare perfectly uniform alloys of any composition containing more than 80 per cent. of silver by re-heating them to about 850° for a number of hours. A practical difficulty in carrying this out would be that the cadmium would be partly volatilised, so that it would be necessary to remove the outer layers of the ingots after heating them.

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* "The Freezing-point of Triple Alloys," 'Chem. Soc. Trans.,' vol. 65 (1894), p. 65.

On the other hand, Osmond has pointed out that it is by no means uncommon for crystallites to be developed by the attack of suitable re-agents in media which are chemically homogeneous. He cites the bronzes and the gold-copper alloys as instances. According to this view the specimens showing crystallites are already uniform in composition and do not require to be annealed in order to become so. It is to be observed, however, that the gold-copper alloys have been shown to be non-homogeneous.* Osmond does not state to what bronzes he refers, but the copper-tin alloys are now well known to be heterogeneous also. It may be repeated that in practice the 92·5-per-cent. alloy is found, on casting, to be uniform in composition, so that it is unnecessary to anneal it.

In the alloys containing from 80—70 per cent. of silver, the crystallites in slowly cooled specimens are larger and more regularly cross- or fern-shaped than in those with more silver (see fig. 4, Plate 10). The matrix is readily dissolved out by nitric acid, leaving the crystallites in relief surrounded by a deep-sunk network. The area occupied by the crystallites is reduced, and that occupied by the matrix increased as the percentage of silver falls. The equilibrium of the systems at lower temperatures has not been examined in this part of the series.

The alloy corresponding to the formula Ag_2Cd is much finer grained than either the 64- or the 70-per-cent. alloy. Etching with nitric acid leaves an excessively fine network in relief with darker pittings between, but no regular structure is observable. Other reagents are equally ineffective in developing the structure. Re-heating at 750° for 1½ hours, and subsequent chilling, merely increases the size of the network without in any other way changing its appearance. One curious effect of heating to 750° these specimens embedded in sand is that the cadmium on the surface is volatilised, leaving a layer of pure silver. On removing this during the operation of polishing, a black layer is encountered coloured by oxide of cadmium, and underneath this the original alloy is found to exist. The layers are not everywhere of the same thickness, so that in the course of polishing alternate rings of white and black are produced, resembling the well-known Japanese decorative metal-work known as Mokumé, which is used in jewellery.

The cooling curves indicate that the compound Ag_8Cd_2 separates from the alloys containing between 50 and 60 per cent. of silver, and this is borne out by the micro-structure. The alloys when rubbed with potassium cyanide solution are seen to consist of white oblong crystals set in a red-coloured matrix (see fig. 5). As the percentage of silver diminishes the area covered by the crystals is reduced, and the amount of matrix increases. The white crystals evidently consist of the compound Ag_3Cd_2, and the red matrix of AgCd.

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* Roberts-Austen and Rose, 'Roy. Soc. Proc.,' vol. 67 (1900), p. 105.

The alloys containing between 50 and 40 per cent. of silver are remarkable for resisting the attack of the ordinary etching reagents. Nitric acid has little effect on them, but they are slowly dissolved by hot acid of a specific gravity of 1·3 without their structure being revealed. A similar lack of success attended the use of sulphuric and hydrochloric acids, of soluble sulphides, of alkaline sulphides with the aid of a galvanic battery, and of heat with free exposure to the air. The alloys are not affected by ammonium sulphide under conditions in which silver-copper alloys or pure silver are instantly tarnished. The structure was developed by a polish attack, which consisted in rubbing the polished specimens on parchment with fine alumina moistened with a solution of 0·5 per cent. of cyanide of potassium. The action is partly abrasive, the red colour being strongly developed in some of the crystals. In the 50-per-cent. alloy, slowly cooled specimens are seen to consist of large crystals of 2—3 mm. in diameter. There is no cementing material, and the crystals are distinguishable from one another under low powers only by their shades of colour. Under high powers (above 1000 diameters) the most strongly coloured crystals are seen to be covered with a number of minute irregular pits and short trenches, which are bright red, the space between being colourless. The difference between the crystals seems to be only that of the orientation of the particles forming them, so that the surface of some crystals is more readily abraded than that of others. The structure, however, is not readily revealed without the aid of the cyanide solution. The abrasions form an irregular network, which gives some of the crystals a minutely cellular appearance, visible at a magnification of 50 diameters. In quickly cooled cast specimens the crystals are much smaller, few being more than 0·3 mm. in diameter, and traces of a hard white cement are discernible between the crystals.

The same alloys when re-heated to 350° for 6 hours and chilled show an even more minute structure, the crystals being only about 0·02 mm. in diameter (see fig. 6). A few hard white projecting grains, probably existing in the alloy after casting and before reheating, are visible under a magnification of 1800 diameters on a slightly pink ground consisting of a solid solution of AgCd and Ag_2Cd_3.

When the 50-per-cent. alloy is heated for 6 hours above 420° and chilled, the separation of the two constituents is far more complete. The alloy is now made up of large bright red hexagonal crystals about

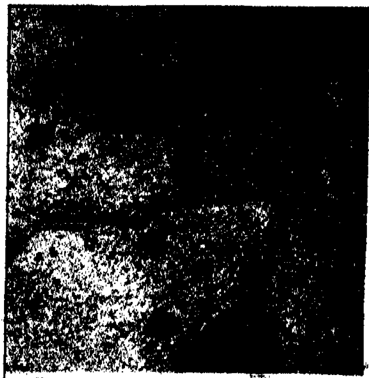

Fig. 3. Silver 92·87%
Cadmium 7·13%
×50 vert.

Fig. 4. Silver 80·5 %
Cadmium 19·5 %
×10 oblique.

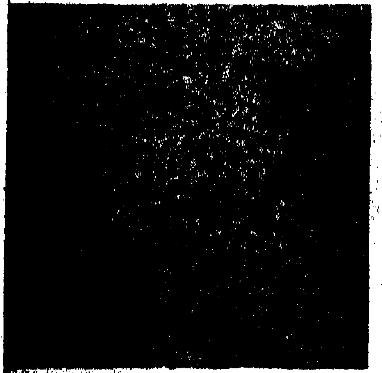

Fig. 5. Silver 55·27%
Cadmium 44·73%
×20 vert.

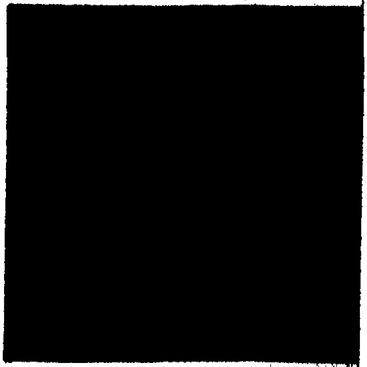

Fig. 6. Silver 50·70% Cadmium [illegible]
Quenched from 350°
×10 oblique.

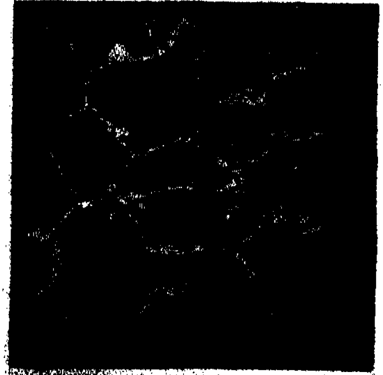

Fig. 7. Same as Fig. 6.
Quenched from 550°
×50 vert.

Fig. 8. Silver [illegible]
Cadmium [illegible]
×50 vertical.

1 mm. in diameter. Near the outside of the specimens these crystals occupy the whole area, but towards the centre the hard white alloy is segregated, forming a cement between the red crystals (see fig. 7). It seems clear that these two constituents are separated at temperatures above 420°, and that the white constituent fuses at that temperature. The white constituent is readily attacked by nitric acid, and may be the compound $AgCd_3$.

The 40-per-cent. alloy, when slowly cooled, is homogeneous and consists of small crystals, about 0·3 mm. in diameter, which become more regular hexagons when re-heated for 24 hours at 350° and chilled, and also when heated at 570° and chilled, but do not increase in size. The alloy remains homogeneous under these conditions, and evidently consists of the compound Ag_2Cd_3.

The portion of the series between the 40- and the 25-per-cent. alloys consists of hard slightly pinkish crystallites of Ag_2Cd_3, set in a matrix which approximately corresponds in composition to $AgCd_3$. The alloys can be etched with nitric acid, and the unattacked crystallites, at first forming almost the whole of the mass, become somewhat rare in the 30-per-cent. alloy, and disappear altogether before the 25-per-cent. alloy is reached.

Specimens containing less than 25 per cent. of silver are much more rapidly attacked by nitric acid than those richer in silver, and when corrosion takes place it is a magma of cadmium with very little silver that is attacked and darkened, leaving the harder white crystallites of $AgCd_3$ practically untouched (see fig. 8). The structure is developed when sections are merely polished, the crystallites of $AgCd_3$ standing out in relief. They diminish in number as the percentage of silver is reduced.

The results of the investigation may be summarised as follows :—

(1) Evidence is afforded of the existence of the compounds $AgCd_3$, Ag_2Cd_3, $AgCd$, Ag_3Cd_2, Ag_2Cd, and Ag_4Cd.

(2) The alloys containing from 0—25 per cent. of silver consist, when solid, of crystals of $AgCd_3$ set in a matrix of cadmium. Those containing between 25 and 40 per cent. of silver consist of the compound Ag_2Cd_3 set in a matrix consisting mainly of $AgCd_3$. The alloy containing about 50 per cent. of silver consists of crystals of a silver-rich body set in a matrix consisting chiefly of $AgCd_3$. The matrix or eutectic solidifies at 420°, or nearly 300° below the freezing point of the crystals.

The alloys containing from 50—60 per cent. of silver consist, at temperatures above 420°, of mixtures of two different solid solutions, one of which is chiefly composed of the compound AgCd, and the other of Ag_3Cd_2. Traces of the eutectic freezing at 420° are still visible.

When more than 80 per cent. of silver is present, the alloys consist of a mixture of two bodies at temperatures between the liquidus and solidus curves, but these unite to form a single solid solution at points on the solidus curve.

(3) The alloys containing over 60 per cent. of silver do not undergo segregation under ordinary conditions, and are practically homogeneous and uniform in composition. They are well suited as a material for the manufacture of trial-plates.

"On the Wetting of Cotton by Water and by Water Vapour."

By ORME MASSON, D.Sc., F.R.S. Received April 25, 1904.

Introduction.

If two thermometers, one of which has its bulb protected by a close covering of ordinary cotton wool, be simultaneously immersed in the same water, all being originally at the same temperature, the protected thermometer shows a marked rise, while the naked one undergoes no perceptible change. Heat is, therefore, generated locally by the wetting of the cotton covering.

The maximum temperature is reached in 2 or 3 minutes, after which there is a fall, the rate of which steadily diminishes in a characteristic manner, so that, when all necessary precautions are taken, a difference of temperature between the cotton and the surrounding water is still distinctly perceptible after several hours. Both the extent of the rise and the rate of the whole change depend on several conditions. With a given thermometer the most important factors are the quantity of cotton wool, its initial condition with respect to hygroscopic moisture, and the temperature of the water. Other things being equal, the effect is more marked with a large covering than with a small one and at a higher than at a lower bath temperature, but the previous condition of the cotton is a more important factor than either. If taken in its ordinary state after exposure to the air of the laboratory, when it usually contains about 8 or 9 per cent. of moisture, it may show a rise of 2° or 3° C., but if precautions be taken to insure that it is dry at the moment of immersion in water (at its own temperature), the same sample will show a rise of from 8—12° or more.

The relatively large amount of air which is always entangled within the cotton wool does not escape during or after immersion, and the bundle presents a glistening appearance under water which suggests that it is not completely wetted. That this fact is important in connection with the observed temperature change is shown by the behaviour of the so-called "medicated" or "absorbent" cotton wool, which differs from the ordinary (nearly pure) material in having been freed by solvents from traces of natural cotton wax. This gives a much smaller rise, and in its case the glistening appearance is absent. Moreover, the quantity of water which penetrates the cotton wrapping and remains mechanically adherent to it and the thermometer when they are lifted out after, say, ½ hour's immersion, may be determined by weighing, and it is found to be less than the weight of the dry cotton in the case of the ordinary material, but several times greater in the case of the absorbent variety. Obviously, therefore, when they are immersed, the former is both better insulated and has the smaller heat capacity, and will thus show a larger rise of temperature for a given heat production, and the observed difference does not necessarily indicate that the absorbent wool is inherently less susceptible to such action as may be the cause of the phenomenon.

The true nature of this action is indicated in the first place by the observation that immersion in water is not essential, for the covered thermometer behaves in a precisely similar manner when exposed to air saturated with water vapour. The rise of temperature is as great or greater, though it may take 5 or 6 minutes to reach the maximum instead of 2 or 3, and the subsequent slow cooling curve is similar, as well as the effects of varying conditions. In fact it has been proved by the experiments to be described that the whole action is essentially the same, whether a bath of water or of saturated air be employed, and that in both cases the heat production is due, at all events, primarily, to the condensation of water vapour on the surface of the cotton fibres. More strictly, this is proved in the case of saturated air immersion, and its extension to the other case is necessitated by the proof of the complete similarity of the thermal changes. In the case of immersion in water the vapour which condenses on the cotton must be produced by evaporation from the liquid, which is prevented from complete contact with the fibres by the air which adheres to them and fills the interstices. There is, therefore, an automatic distillation from the water on to the cotton which acts as a condenser, and the heat gained there must be matched by an equal loss of heat by the adjacent water, though the large heat capacity of the latter prevents any fall of temperature comparable with the observed rise. "Absorbent" cotton wool is found to behave in saturated air exactly like the ordinary variety, in contrast with its much smaller temperature effect in water. This is in complete accord with the theory. The condensation of vapour that occurs during exposure to saturated air never renders the cotton sensibly moist, though it may absorb over 20 per cent. of its weight in a few hours.

It has long been known that rise of temperature results from the immersion of finely divided solids in water and other liquids. Pouillet* examined a large number of substances, both inorganic and organic, and showed that the property is a general one, that the state of division and previous dryness of the material are important, and that the phenomenon is much better marked with animal and vegetable substances than with mineral powders. His experiments, however, can hardly be regarded as quantitative, for the temperature rises, of which he records a long list, have no real significance apart from the special conditions under which they were observed, nor do they by themselves throw light on the nature of the process which causes them. Later observers seem to have confined their attention to inorganic materials such as silica and glass, and the recent work of G. J. Parks, which will be referred to later, is specially notable in this connection. But the author is not aware of any previously recorded thermometric investigation on the lines he has adopted, having the following objects in view :—

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* 'Ann. de Chim. et de Phys.,' 1822, (2), vol. 20, pp. 141—162.

1. To map the whole course of the observed change of temperature of cotton due to its immersion in water, tracing both the rise to the maximum and the subsequent fall.
2. To do the same for the case of immersion in air saturated with water vapour, and to compare the two results.
3. To examine the effect of varying conditions and particularly of the initial dryness or dampness of the cotton.
4. To determine, in the case of immersion in saturated air, the course of the hygroscopic absorption.
5. To ascertain the relation between this absorption and the temperature change.
6. To examine the information so obtained as to its bearing on the nature of the Pouillet effect.

Apparatus and Methods.

The *thermometers* required to fulfil the two conditions of being short enough to be weighed on an accurate balance and of yet having a sufficient length of scale. As they were likely to be used at various temperatures, a very open scale was out of the question. Those chosen were graduated in whole degrees only, reading from below zero to 100° C. Readings were always made by a telescope with a micrometer scale in the eyepiece. In all the earlier experiments this micrometer scale was used merely for subdividing the degrees, but in those described as Series V it was employed so as to make the readings altogether independent of the thermometer graduations.

Comparison of the instruments with a standard thermometer at various temperatures showed that the capillary was of practically uniform bore, and as all the readings in any experiment were referred to the initial one, so as to give temperature differences, any zero-point error of the thermometer was of no importance.

The *telescope* was generally so placed that one division of the micrometer scale was equal to 0°·2, and readings were taken to 0°·02. They may, in the case of Series V, be taken as free from errors as large as 0°·05, but the earlier observations are less reliable for the reason stated. The actual temperatures of the immersion bath, as given in the tables, were ascertained by a standard thermometer that could be read to 0°·01, and in all experiments after Series II these temperatures were maintained constant to within 0°·03 by a thermostat.

The experimental thermometer was provided with a *jacket tube* of sufficient length to enclose the bulb and part of the stem, and a smooth red-rubber cork was fixed at such a position on the stem that the tube, when in use, was closed and air-tight. All that part of the scale which was used in the observations lay above the level of the cork, and there was sufficient length below it to admit of proper immersion of the bulb and cotton covering without submerging the cork itself. The thermometer was provided with platinum loops so that it could, with its tube, be slung slantwise on the balance for weighing.

The *cotton wool* was tightly wound round the bulb so as to efficiently cover it and a small part of the stem, leaving enough room between it and the cork for subsequent operations. From ½—1 gramme was found to be a convenient quantity. When once properly wound it remains in position without any special fastening, but for a long series of experiments it is safer to secure it with a single turn of cotton thread. After winding, it should be hung in distilled water for a day to remove soluble impurities derived from the fingers or the laboratory air, and should not afterwards be touched.

In the latter experiments (Series V) a *duplicate thermometer* with cork and tube, but without cotton wool, was used as a counterpoise in weighing, and was also put through every treatment in the same way and at the same time as the experimental apparatus. It was hoped by this means to minimise any small errors that might result from hygroscopic changes in the weight of the rubber cork.

The *oven* used for drying the cotton covering before any experiment was an ordinary air bath with temperature regulated to about 110° C. and with a fairly free draught passing through it. The bulb of the thermometer passed through an opening in the roof, and a slotted wooden cover supported the rubber cork outside the bath and protected it from the heat. It was proved that an hour's drying was more than enough to give constant weight.

It may be mentioned here, as a curiously extreme instance of the ordinary wet and dry bulb effect, that the experimental thermometer with its covering, when lifted out of cold water and placed in the oven, rises steadily till it reaches a point some 50° or 60° below the oven temperature, then oscillates for some time about that point (following the oscillations of the gas regulator) and finally rises steadily to the full temperature. The effect is seen best when absorbent wool is used, as it carries a much larger store of water.

The *immersion bath* varied according to circumstances. In Series II, for water immersion, it was simply a glass jar holding about 3 litres of distilled water. Its temperature was that of the laboratory and was thus not the same throughout the series, but it varied only between 16° and 18°, and during any one experiment it did not alter more than a few tenths of a degree. This last variation was recorded and afterwards approximately corrected for, in plotting the temperature curve of the covered thermometer. The results are, of course, though fairly good, less reliable than those of later series; for in all of these the immersion bath was placed in a thermostat which kept constant to within 0·03. In the later water immersion tests the bath was a wide-mouthed thin glass flask containing distilled water, and it was clamped in the thermostat so that only its open mouth was above the surface of the water in the latter. For immersion in air saturated with water vapour, this flask was replaced by another arrangement which underwent some modification as the work proceeded. In Series III a large wide-mouthed glass bottle was used, with a layer of water at the bottom and with an air current passing through it. This air was previously saturated at the right temperature by passing through a lead worm and a wash-bottle, both submerged in the thermostat, and it was then delivered into the bottle through a tubulated neck near the bottom. In Series IV the air current was sent through additional saturators, and a cover was provided for the bottle so as to close it when in use, except for the opening which admitted the thermometer. In Series V, as some doubts were entertained as to perfect saturation in previous tests, the bottle was replaced by a large cylindrical pot of porous earthenware, with a hole near the bottom through which the air current could be conveyed. The pot was very completely surrounded by the water of the thermostat and was provided with perforated card covers. The infiltration of water through the walls kept the whole inside surface wet and provided a large and constant area of evaporation. At the same time the infiltration was not rapid enough to give any trouble, even in protracted experiments, if the pot was emptied by a syphon at the start. With this arrangement it was found that it made no appreciable difference whether the air current was used or not, and it was not used in the last six experiments of the series.

Hooks, which occupied a fixed position with respect to the telescope so that its distance and the value of its scale did not vary, served for the vertical suspension of the thermometers during immersion. The small water motor which worked the stirrer of the thermostat was connected with the same support as these hooks, and at each rotation of the belt a slight jolt was thus given to the thermometers which served the purpose of an automatic tapper in preventing the mercury from sticking.

The actual conduct of an experiment is as follows:—The covered thermometer is dried at about 110° for an hour as already described, the jacket tube being placed separately in the oven at the same time. The counterpoise thermometer and tube, if used, are treated similarly in this and in all subsequent operations. The instrument is then removed and quickly inserted into its tube, both being well above 100°, and is left to cool to the temperature of the balance. Its weight is taken after a momentary loosening of the cork to equalise pressure, and it should not vary in a series of tests more than about 0·001 gramme from the mean. In the twenty experiments of Series V, where the duplicate instrument was used as a counterpoise, the variation was only half as much. The weight of the dry wool itself may be obtained by deducting the tare of the instrument, taken before the bulb was covered.

The thermometer, still protected by its tube, is then suspended in the immersion vessel (water or saturated air as the case may be) and the cover put on, and readings are taken by the telescope from time to time till their constancy indicates that the covered bulb has reached the fixed temperature of the thermostat. About an hour suffices. The final reading is noted as the initial temperature of the experiment. The thermometer is then as rapidly as possible withdrawn, removed from its tube, and re-hung in the proper position, and a stop-watch is started at the moment of immersion. The cover is replaced, the telescope is adjusted vertically so that its scale occupies exactly the same position as before with respect to a fixed mark on the thermometer, and readings begin. These are taken at short intervals, and always, except at the maximum temperature and at the finish, at the moment when the mercury is crossing a scale line, the time being noted to the nearest second so long as seconds are of any importance.

Generally the experiment is stopped at an exact pre-appointed time by removing the thermometer as rapidly as possible to its jacket tube, and it is then allowed to take the temperature of the balance and weighed. The difference between this and the original dry weight gives the amount of moisture absorbed during the immersion. As the final temperature cannot be read at the actual moment of stoppage, a very slight extrapolation is generally necessary to complete the curve; for the exact final temperature may be wanted for a purpose that will appear later. Of course, in the case of water immersion the weighing is omitted, as absorbed moisture cannot be distinguished from that which mechanically adheres to the cotton.

At the completion of an air immersion experiment, after the instrument has been weighed, it may be at once used for a second experiment in which the influence of a known amount of previous moisture is observed, the procedure being similar to that already described. In Series II (water immersion tests) previous moisture was given to the cotton in roughly predetermined quantity by exposing it for suitable times in moist air at the ordinary temperature.

To obtain the curve which shows the progress of absorption of moisture during immersion in air saturated at any fixed temperature, it is necessary not only to accurately maintain the bath at that temperature but to guard against any interference with the temperature of the cotton. It is an essential feature of the process that the cotton shall become hotter than the bath, and the velocity of absorption at any moment must be affected by the magnitude of this difference of temperature. It is, therefore, impossible to trust an absorption curve obtained from one long experiment, interrupted from time to time for the purpose of weighing. After each such interruption the cotton resumes operations at a lower temperature than that at which it left off, and moreover it never again gets back exactly on to its original temperature curve. There are other errors also which result from such a method, but they are of less importance. Therefore the plan was adopted of determining each point on the absorption curve by means of a separate experiment, starting always with dry cotton, and immersing it for different times, but keeping all other conditions the same. The temperature curve was taken simultaneously in each test.

Unfortunately it has not been found possible to so arrange things that each temperature curve follows the exact course of the last, which would be the best proof of the trustworthiness of the absorption curve. The differences, though small, are unmistakable even in the case of Series V, which was the best in several respects. The extent of these discrepancies will be shown in the tables summarising results. The cause of them is not to be found in the drying process, as is proved by the uniformity of dry weight; nor in premature absorption through the corks after weighing, as this was disproved by special tests; nor in incompleteness of saturation of the air, nor in any other circumstance peculiar to the air immersion experiments, for similar small variations occurred in the temperature curves got by water immersion. It is probable therefore that the errors arise at the moment the thermometer is withdrawn from its tube at the start of each experiment, and that this exposure to air of variable temperature and moistness, brief though it is, initiates a disturbance that shows itself later in the manner described. It is not easy to devise a remedy that would not introduce troubles of its own. Finally it may be pointed out that the constancy of the bath temperature, and the fact that the cotton is always hotter than the bath, afford security against any error such as might otherwise be caused by deposition of dew.

Experimental Results.

In what follows and in the curve diagrams—

t is the time measured in minutes from the moment of immersion of the cotton-covered thermometer;

θ is the temperature of the same at the moment t, in degrees Centigrade, its own initial temperature, which is the constant temperature of its environment, being taken as zero;

ϕ is the maximum value attained by θ in the course of the experiment;

τ is the value of t at which $\theta = \phi$;

m is the weight of water vapour, in milligrammes, absorbed in the time t;

p is the weight of any water vapour, also in milligrammes, absorbed by the cotton prior to the commencement of the experiment;

A is the area, determined by planimeter, bounded by the curve, the t axis, and a vertical ordinate corresponding to the time t; or $A = \int_0^t \theta dt$.

The terms "water immersion" and "saturated air immersion" have already been fully explained. "Previous moisture" serves to designate that of which the quantity is p. The term "dry curve" is used to distinguish one belonging to an experiment in which the cotton is dry to start with from those which show the effect of previous moisture.

It is unnecessary to reproduce here the numerous t and θ readings of the experiments. They are therefore summarised in the following tables, giving the values of τ and ϕ, the final values of t and θ, and the corresponding values of A and m (where determined), and the value of p in cases where previous moisture was present. In Tables III and V calculated values of m are given also. The mode of calculating m from A and θ will be explained later. Some of the curves are shown in the diagrams, and references to these are given in the tables.

The experiments which formed Series I were of a purely preliminary character, and are therefore omitted. Those of Series II were, as already explained, less accurate than later ones; but they are correct enough for their purpose, for they show by comparison with Series III the general similarity of the temperature change produced by water immersion and by saturated air immersion, both with and without previous moisture. Series III also gave information as to the progress of absorption during exposure to saturated air; and the main purpose of Series IV and Series V was to trace this more fully in connection with the temperature change. They also supplied some evidence as to the influence of bath temperature and weight of cotton. Finally water immersion tests, carried out in conjunction with Series IV and V, gave temperature curves capable of accurate comparison with those of saturated air immersion under otherwise identical conditions. The experiments of Series V are probably more exact than any of the others, for reasons already explained.

Table I.—Summary of Series II.

0·55 gramme of cotton wool covering thermometer C. Water immersion at 16—18°. τ = 3 to 3½ minutes.

Order of experiment.	Approximate bath temp.	p.	ϕ.	θ at 30 minutes.	Reference to figure.
1	17°·0	0	8·3	1·7	
5	18·0	0	1·55	1·75	Fig. 1, *a*.
11	17·3	0	8·65	1·8	
6	17·3	9	7·4	1·7	
3	17·7	18	6·15	1·55	Fig. 1, *b*.
7	17·0	24	4·95	1·5	
4	16·7	33	3·45	1·35	Fig. 1, *c*.
2	16·1	44	2·3	1·2	
8	16·8	53	1·65	1·05	
12	18·2	68	1·1	0·7	Fig. 1, *d*.
9	17·2	88	0·6	0·55	
10	17·4	101	0·4	0·35	

Table II.—Summary of Series III.

0·53 gramme of cotton covering thermometer C. Saturated air immersion at 18°·0. τ = about 6 minutes, slightly increasing with p.

Order of experiment.	p.	ϕ.	t.	θ.	m.	Reference to figure.
2	0	8·65	6	8·65	17·6	
7	0	8·75	6	8·75	17·8	
3	0	8·8	15	6·8	32·5	
4	0	8·8	35	3·05	48·3	
5	0	8·8	64	1·65	62·7	Fig. 2, *a*.
6	0	8·7	111	0·95	77·8	
1	0	8·65	185	0·7	98·6	
8	0	8·8	307	0·3	108·0	
2A	17·6	6·15	73	1·2	52·4	Fig. 2, *b*.
3A	32·5	3·85	73	1·15	41·3	Fig. 2, *c*.
4A	48·3	1·95	70	1·0	28·4	
5A	62·7	1·15	70	0·75	19·7	Fig. 2, *d*.
5B	82·4	0·6	72	0·5	12·6	

Under t, in this and the following tables, is given the time at which each experiment was concluded; and the corresponding values of θ, A, and m, are given in the appropriate columns.

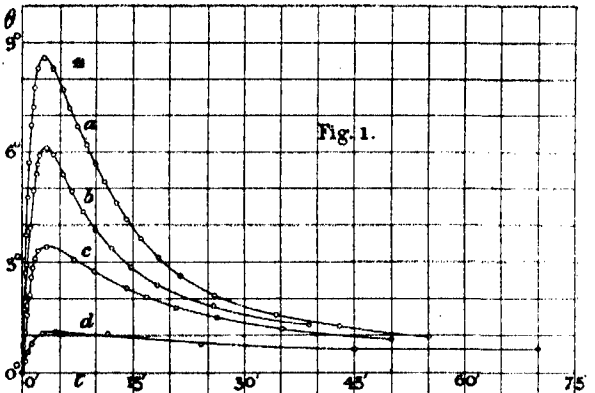


Fig. 1.

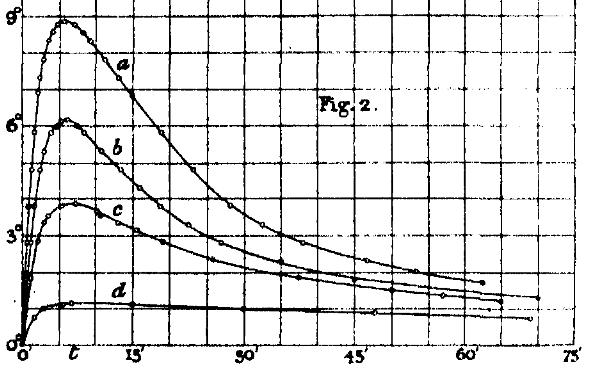


Fig. 2.

Description of Curve Diagrams, figs. 1—4.—Curves showing change of temperature by cotton while absorbing moisture. Time (t) expressed in minutes. Temperature of cotton (θ) in Centigrade degrees, its initial temperature and the constant temperature of the immersion bath being taken as zero. (See Tables I, II, III and IV.)

Fig. 1.—Immersion in water at 16° to 18° C. Cotton = 0·55 gramme.

(a)	Originally dry.				
(b)	Containing	18	milligrammes	of previous	moisture.
(c)	„	33	„	„	„
(d)	„	68	„	„	„

Fig. 2.—Immersion in saturated air at 18°·0. Cotton = 0·53 gramme.

(a)	Originally dry.				
(b)	Containing	17·6	milligrammes	o previous	moisture.
(c)	„	32·5	„	,	
(d)	„	62·7	„	„	

Table III.—Summary of Series IV.

0·53 gramme of cotton covering thermometer C. Saturated air immersion, with better arrangements than in Series III. Bath temperature 18°·0. τ = about 5½ minutes.

Order of experiment.	*p*.	*φ*.	*t*.	*θ*.	A.	*m*.	*m* (calcd.).
7	0	Not reached	8	7·93	14·8	12·2	11·6
5	0	8·85	6	8·85	40·2	19·9	18·9
6	0	8·75	15	6·42	109·7	33·3	33·8
2	0	8·87	16	6·12	117·5	35·7	35·5
1	0	8·78	30	3·30	180·6	48·7	48·4
4	0	8·95	35	2·70	197·0	51·3	51·9
8	0	8·90	50	1·82	226·4	57·5	58·4
3	0	8·90	65	1·39	252·4	65·0	64·5
7A	12·2	6·92	6	*φ*	—	16·4	—
5A	19·9	5·90	6	*φ*	—	13·5	—
6A	33·3	3·32	6	*φ*	—	9·2	—
4A	51·3	1·73	6	*φ*	—	5·3	—
3A	65·0*	1·00	6	*φ*	—	3·6	—

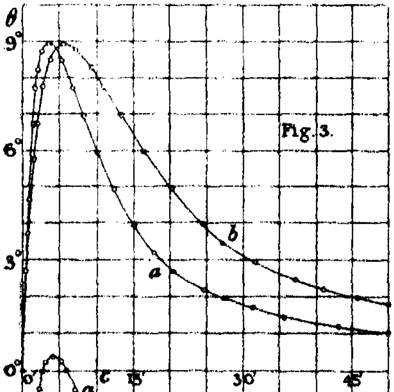


Fig. 3.—Immersion at 18°·0 of 0·53 gramme of dry cotton.

(*a*) In water.
(*b*) In saturated air.

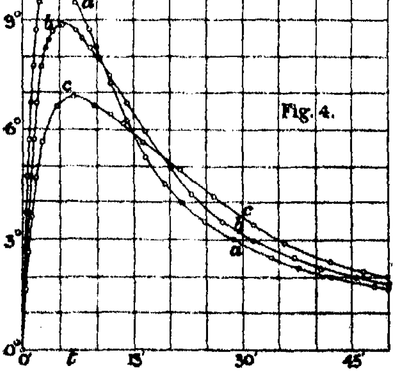


Fig. 4.—Immersion of 0·53 gramme of dry cotton in saturated air.

(*a*) At 25°·0.
(*b*) At 18°·0.
(*c*) At 12°·0.

The temperature curve of Experiment 8 is shown in fig. 3*b*, where the companion curve (*a*) represents a water immersion experiment under otherwise similar conditions.

In fig. 4, the temperature curves are shown as obtained by immersing the dry cotton in air saturated at (*a*) 25°, (*b*) 18°, (*c*) 12°, so as to test the effect of the greater vapour pressure. The following table summarises these additional tests.

Table IV.—Experiments Supplementary to Series IV, and with same Apparatus.

Experiment 3 of Series IV included for comparison. No previous moisture.

Immersion.	Bath temp.	τ.	φ.	t.	θ.	m.
Water..............	18°·0	3·5	8·90	65	0·78	—
Saturated air........	25·0	4·3	10·40	65	1·30	69·2
,, ...	18·0	5·5	8·90	65	1·39	65·0
,, ...	12·0	6·9	6·90	65	1·47	55·4

Table V.—Summary of Series V.

0·90 gramme of cotton covering thermometer D. Saturated air immersion with improved arrangements. Bath temperature 25°·0. τ = about 5½ minutes. No previous moisture. For θ and m curves, see fig. 5.

Order of experiment.	ϕ.	t.	θ.	A.	m.	m (calcd.).
7	Not reached	2·35	10·07	12·8	15·7	14·5
10	12·8	5·35	12·8	48·8	28·5	26·8
2	12·8	5·5	12·8	51·0	27·4	27·3
3	12·62	10	10·95	104·5	39·3	39·3
16	12·62	10	11·25	103·6	39·4	39·3
4	12·50	18	7·60	177·4	53·0	54·5
5	12·68	18	7·57	178·9	53·8	54·8
12	13·00	18	7·77	183·4	55·7	56·2
1	12·68	30	4·73	258·0	72·6	71·0
6	12·58	30	4·44	245·5	68·5	68·7
15	12·68	30	4·70	252·4	68·8	70·8
8	12·63	45	2·95	300·0	80·9	81·3
9	12·58	60	2·18	339·4	90·2	90·6
11	12·80	80	1·74	382·5	103·8	101·4
13	12·80	80	1·68	382·0	108·7	101·2
14	12·80	80	1·82	393·1	101·7	104·2
17	12·54	120	1·12	425·8	114·7	112·0
18	12·80	180	0·85	508·8	130·8	133·2
19	13·00	360	0·40	608·8	159·8	158·7
20	12·72	720	0·22	723·3	187·9	188·3

The Temperature Curve.

In all the experiments this curve is obviously of such a form that, for any given value of θ, there are two t values, say t_1 on the ascending slope, and t_2 on the descending slope; and when θ has its maximum value $(= \phi)$ $t_1 = t_2$ $(= \tau)$.

Inspection of any of the curves representing experiments in which previously dry cotton was immersed, either in water or in saturated air, brings out two relations which hold good with approximate accuracy. The first is that the two times for any given θ vary inversely as one another, or

$$t_1 t_2 = a \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(I)},$$

a being necessarily equal to τ^2.

The second is that θ varies inversely as the sum of its two times, or

$$\theta(t_1 + t_2) = b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(II)},$$

and the value of b is necessarily $2\tau\phi$.

Selecting Experiment 20 of Series V to illustrate these rules, we find that a does not vary more than about 2 per cent. on either side of the value 30·8, and that b, which is 141·2 when θ is at its maximum, rises as θ falls to about 152 and then falls again towards its original value. Similar, and sometimes greater, deviations from constancy are shown in all the experiments.

Equations (I) and (II) can evidently be combined to give one which approximately characterises the whole curve, viz.:

$$\theta(t + a/t) = b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(III)},$$

where t is any time, θ has the corresponding value, and a and b must have the values already assigned to them, viz., $a = \tau^2$ and $b = 2\tau\phi$. It follows that the whole course of any such curve is definable in terms of the special values assumed by τ and ϕ. In other words, a "law of corresponding states" is arrived at, which may be most simply expressed by giving to Equation (III) the form $2\theta/\phi = t/\tau + \tau/t$, or may be put in words as follows:—

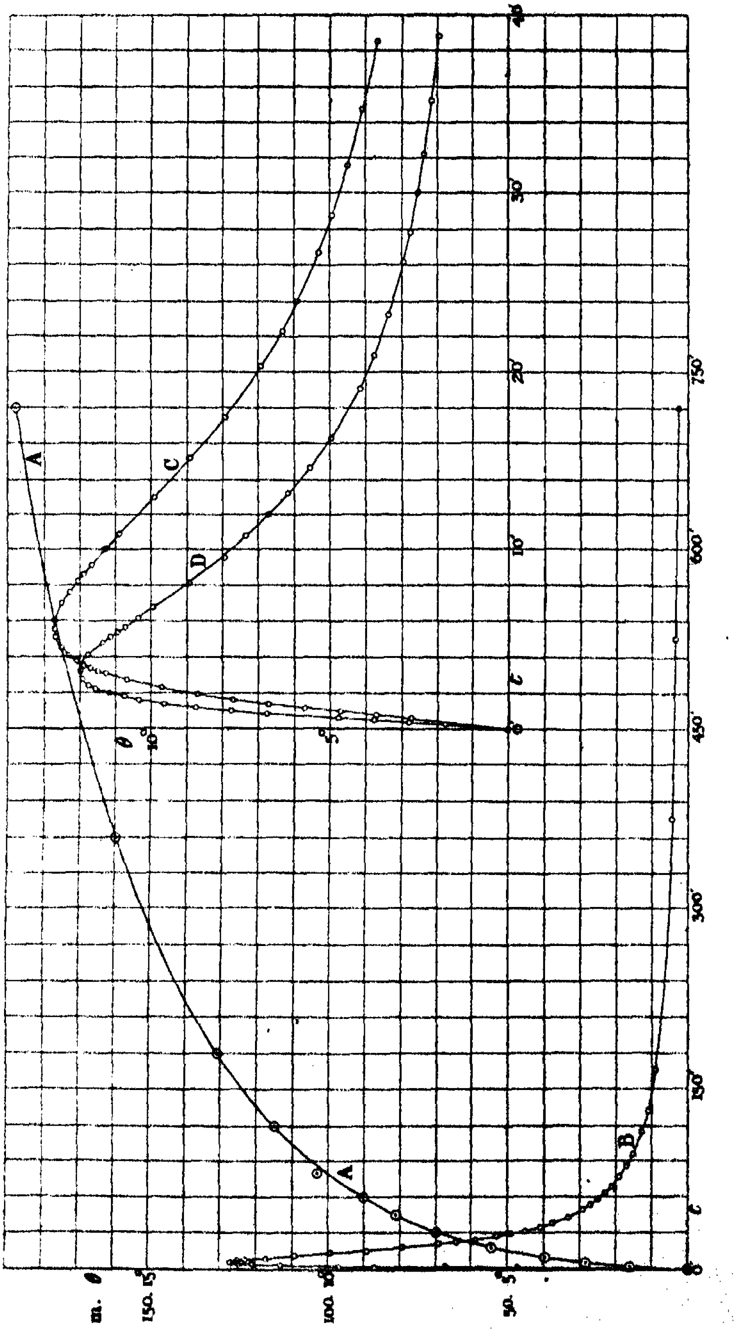
The temperature curves for all experiments, whatever the conditions, should be superimposable if in each case the θ values are expressed as fractions of ϕ and the t values as fractions of τ.

This suggests a method for comparing the curves for water immersion and saturated air immersion more exactly than can be done by mere inspection. The results are shown in Tables VI and VII. In each of these the fourth column contains the same selected values of θ/ϕ, and the first column contains the corresponding actual values of θ. The figures in the second and third columns respectively show the times at which these θ values are obtained on the ascending and descending slopes of the curve, and the fifth and sixth columns show the corresponding values of t/τ. All the θ and t values may be taken as experimental numbers, having been found by careful interpolation from the recorded readings. ϕ is the result of actual observation; but τ is from its nature not sharply defined, for the temperature always remains sensibly constant at its highest point for a considerable fraction of a minute. The values of τ used in the tables, and shown at the head of the second and third columns, were therefore obtained by plotting the arithmetic means of t_1 and t_2 for θ values in the immediate neighbourhood of ϕ and then slightly extrapolating the curve so formed. No appreciable error is introduced by treating this short portion of the curve as a straight line, though in fact it is part of a rectangular hyperbola. Practically the same τ value is obtained by assuming that it is the geometric mean of the t_1 and t_2 of any closely contiguous θ value. The τ so found is of course well within the limits prescribed by actual observation.

For the comparison of saturated air immersion with water immersion, the figures in the fifth and sixth columns of Table VI should be read together with the corresponding figures of Table VII. The differences are such as would be accounted for by comparatively small experimental error, and are indeed not greater than might occur in a similar comparison of two saturated air tests. The results point therefore to the identity of the effects, and so of the causes at work, in the two cases.

For a comparison of either case with the results indicated by the Equation (III), the figures in the last four columns of Tables VI and VII may be read with the calculated values shown in Table VIII. It is evident that there are greater differences between the calculated and found values than between the found values of saturated air and of water immersion, and that the tendency in both cases is for the smaller t/τ to be in practice a little too small, and the larger t/τ to be a little too large for the theory, while their product still remains of practically unit value, as indicated by the equation. Such differences are somewhat more strongly marked when the experiments at the lower bath temperature (18°) are studied in the same way; but here, again, the close similarity between the water and saturated air tests is conspicuous. Whether the agreement between the equation values and those of the experiments would be improved by elimination of such errors as may arise from the short initial exposure of the cotton to outside air, from the lag of the thermometer, or from other causes (some of which may work in opposite directions), it is impossible to say without further data.

Fig. 5.


A
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***Description of Fig.* 5.**—Curves showing behaviour of 0·90 gramme of cotton originally dry. Bath temperature, 25°·0 in all cases. (See Tables V, VI and VII.)

A. Absorption curve in saturated air bath up to 12 hours. Moisture absorbed (m) in milligrammes.

B. Temperature curve corresponding to A.

C. The early part of curve B on an enlarged time scale.

D. Temperature curve obtained by immersion in water; otherwise same as C.

Table VI.

Saturated air immersion at 25°. 0·90 gramme of cotton.

θ.	t_1.	t_2.	$\frac{\theta}{\phi}$.	$\frac{t_1}{\tau}$.	$\frac{t_2}{\tau}$.	$\frac{t_1 \times t_2}{\tau^2}$.	$\frac{\theta\,(t_1+t_2)}{2\tau\phi}$.
12·72	5·55	5·55	1	1	1	1	1
12·08	3·78	8·27	0·95	0·68	1·49	1·01	1·03
11·45	3·22	9·70	0·9	0·58	1·75	1·01	1·05
10·18	2·50	12·37	0·8	0·45	2·23	1	1·07
8·90	2·07	15·17	0·7	0·37	2·72	1·01	1·08
7·63	1·65	18·25	0·6	0·30	3·29	0·98	1·08
6·36	1·37	22·10	0·5	0·25	3·95	0·98	1·05
5·09	1·08	27·85	0·4	0·19	5·02	0·98	1·04
3·82	0·85	37·3	0·3	0·15	6·72	1·03	1·03
2·54	(0·56)	56·6	0·2	(0·10)	10·2	—	1·03
1·27	(0·28)	117·2	0·1	(0·05)	21·1	—	1·06

Table VII.

Water immersion at 25°. 0·90 gramme of cotton.

θ.	t_1.	t_2.	$\frac{\theta}{\phi}$.	$\frac{t_1}{\tau}$.	$\frac{t_2}{\tau}$.	$\frac{t_1 \times t_2}{\tau^2}$.	$\frac{\theta\,(t_1+t_2)}{2\tau\phi}$.
12	3·20	3·20	1	1	1	1	1
11·4	2·15	4·72	0·95	0·67	1·48	0·99	1·02
10·8	1·82	5·62	0·9	0·57	1·76	1	1·04
9·6	1·43	7·25	0·8	0·45	2·27	1·01	1·09
8·4	1·13	9·03	0·7	0·35	2·82	1	1·11
7·2	0·93	11·1	0·6	0·29	3·47	1·01	1·13
6	0·77	13·7	0·5	0·24	4·28	1·03	1·13
4·8	0·60	16·8	0·4	0·19	5·25	0·98	1·09
3·6	0·47	21·8	0·3	0·15	6.81	1	1·04
2·4	(0·32)	31·6	0·2	(0·10)	9·88	—	1
1·2	(0·16)	66	0·1	(0·05)	20·6	—	1·04

Table VIII.—Values Calculated from the Equation $\theta\left(t+\frac{a}{t}\right) = b$.

$\frac{\theta}{\phi}$.	$\frac{t_1}{\tau}$.	$\frac{t_2}{\tau}$.	$\frac{t_1 \times t_2}{\tau^2}$.	$\frac{\theta(t_1+t_2)}{2\tau\phi}$.
1	1	1	1	1
0·95	0·72	1·38	1	1
0·9	0·63	1·60	1	1
0·8	0·50	2·00	1	1
0·7	0·41	2·45	1	1
0·6	0·33	3·00	1	1
0·5	0·27	3·73	1	1
0·4	0·21	4·79	1	1
0·3	0·15	6·51	1	1
0·2	0·10	9·90	1	1
0·1	0·05	19·95	1	1

One characteristic feature of the temperature curve in every case, and well shown in fig. 5, B, is the rapid approximation of the cooling portion to the form of a rectangular hyperbola. This is indeed indicated by Equation (III), since, when t is large enough a/t is practically negligible, and $\theta t = b$. The temperature of the cotton, therefore, cannot in any finite time return absolutely to that of its environment. This points, also, to there being no finite limit to the vapour absorption process which is the cause of the heat supply—a result which will be discussed later. Meantime, it may be noted that both the temperature effect and the progress of absorption are still distinctly manifest after 12 hours, and could certainly be followed for days if necessary.

The temperature curves showing the effects of previous moisture (figs. 1 and 2) may evidently be regarded, in respect to their down slopes, as representative of later portions of the dry curve, for they could take their origin from such times as would account for the absorption of so much previous moisture in the same environment. Thus the curves *b*, *c*, *d* (fig. 2) would start at 6, 15, and 64 minutes respectively. Even then, however, the new curve would at its highest point fall below the original one, and the two would never really coincide afterwards. Thus a permanent interference with the normal course of the temperature is caused by interrupting the absorption process, and again resuming it after the cotton has cooled in its closed tube, and this must naturally react to some extent on the subsequent absorption rate.

The Absorption Curve.

The best and most numerous *m* data are those for Series V (Table V), and the curve for these is shown in fig. 5, A. In plotting it, the mean *m* value has been used in cases where there was more than one determination. The curves for earlier series are similar, as far as they go. The absorption occurs rapidly at first, and proceeds with diminishing velocity, but the evidence does not point to even practical finality being reached for many days, and there is no theoretical limit to the process. Like the θ curve, that for dm/dt would evidently show an asymptotic approach to the t axis. For comparison, the complete θ curve for the 12-hour experiment of the series is shown on the same plate (B) as the m curve (A). It is very evident that the moment of maximum temperature marks but a small advance in the progress of absorption, and that the heating effect of the latter must be continuous throughout, and would continuously raise the temperature if not counteracted.

Relation of the Temperature, Time, and Absorption Values.

The net rate of gain or loss of heat by the covered thermometer at any moment must depend upon both the rate at which it is receiving heat from the vapour condensation, and the rate at which it is losing heat by radiation, convection, and conduction. If it be assumed (1) that the heat received is directly proportional to the weight of moisture condensed, (2) that the rate of loss of heat due to the above causes is directly proportional to the difference of temperature between the thermometer and its environment (assumptions which the results will justify later), it follows that

$$dm/dt = c\theta + k\,d\theta/dt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(IV)},$$

where m, t, and θ have the same significance as before; c is the normal heat loss by the covered thermometer, due to radiation, etc., per unit θ per minute; k is the heat capacity of the same, *i.e.*, of the cotton and that part of the thermometer which is directly affected; and the unit of heat adopted is that quantity which is rendered available by the absorption of 1 milligramme (unit m) of moisture by the cotton.

From Equation (IV) it follows by integration that $m = c\int_0^t \theta dt + k\theta$, or for brevity,

$$m = cA + k\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(V)},$$

a result which is manifest when it is considered that the total heat received by absorption from the beginning of any experiment up to any stated time is represented in part by the total heat lost within that time, and in part by the amount still retained by the covered thermometer in excess of its original heat contents, and also that the total heat lost is proportional to the average θ and the whole time, the product of which is A.

It is evident that, while c is a constant (by hypothesis) throughout any series of tests performed under similar conditions, k is from the very nature of the case a variable; for it must increase gradually in proportion to the vapour absorbed. As a fact, however, it will be shown that the error arising from a neglect of this increase of k in the application of Equation (V) is negligible, provided that its value near the beginning of the experiment be fairly correctly estimated; for it is only at this end that $k\theta$ is at all large in comparison with cA, and by the time that k has undergone any noteworthy increase $k\theta$ itself may be regarded as a mere correction.

The values of c and k may be deduced from the experiments themselves in the following manner:—In the first place, since at the turning point (when $\theta = \phi$ and $t = \tau$) $d\theta/dt = 0$, it follows from Equation (IV) that here $c\theta = dm/dt$. This value of dm/dt can easily be got with fair accuracy by measuring the slope of the m curve at the time τ: hence, c is approximately determined. But a more exact value can be obtained by measuring A for a long experiment in which θ has become a mere fraction of 1° and A is very large, so that $k\theta$ may be fairly neglected in Equation (V). The value of c being fixed, that of k (taken as constant) follows by applying this equation to experiments of short duration. The following case serves for illustration:—The m curve for Series V, in which $\tau = 5·55$ and $\phi = 12·72$, gave about 3·1 as the value of dm/dt at 5·55 minutes; hence, $c = \frac{3·1}{12·7} = 0·25$ approximately. Experiment 20 of the series showed $m = 187·9$ in 720 minutes, when θ was only 0·22 and A was 723·3; hence $c = \frac{187·9}{723·3} = 260$. This last value was found to give very consistent results in the other experiments if k were taken as having the value 1·1. The figures in the column headed m (calcd.) in Table V were got from these values of c and k. In the case of Series IV (Table III), where a different thermometer and less cotton were used, and where the atmosphere of the bath (saturated at 18° instead of 25°) was less moist, slightly different figures were required, viz., $c = 0·25$ and $k = 1·0$

If the θ curve were rigorously defined by Equation (III), it would follow that $\mathrm{A} = \frac{b}{2}\, log_e \frac{t^2+a}{a}$ and $\theta = \frac{bt}{t^2+a}$, so that m could be calculated from the time by the equation

$$m = \frac{bc}{2} \log_e \frac{t^2+a}{a} + kb\,\frac{t}{t^2+a},$$

which involves the three constants, a ($= \tau^2$ of the θ curve), $\frac{1}{2}bc$, and kb. As a matter of fact, a very fair approximation to the actual m values may be got in this way, though the agreement is not quite so good as when the measured A and θ are used, in which latter

case also the calculation is independent of any purely empirical formula.

The Influence of the Bath Temperature.

The only experiments designed to test this question were those summarised in Table IV and illustrated in fig. 4. The θ curves are there seen to cross one another on the down slope in such a way as to suggest that the rates of absorption, originally higher at the higher bath temperature, reverse their order of magnitude not long after passing the maximum θ. This conclusion would necessarily follow from Equation (IV) if c were a constant for the three experiments at 12°, 18°, and 25°, for then $c\theta$ must be equal for any pair at the moment of crossing, and $kd\theta/dt$ is manifestly of larger negative value there for the curve belonging to the higher bath temperature. But c, though essentially a constant unaffected by temperature, is known to be susceptible to change if the amount of water vapour in the air be altered, as is the case in passing from an experiment at one bath temperature to one at another, and, as a matter of fact, measurement of the areas of the θ curves for 12°, 18°, and 25°, and comparison of them with the actual m values at 65 minutes, show that c must be given the approximate values 0·22, 0·25, and 0·27 respectively. And when this difference is allowed for, it appears that the rates of absorption in the three experiments originally different approach the same value, but do not reverse their order. For a proper investigation of this question complete series of experiments would be required at different bath temperatures, all other conditions being the same.

Magnitude of the Heat Development.

In the preceding tables there is sufficiently good agreement between the found and calculated values of m to justify the statement that the two assumptions on which the calculation is based are substantially correct. It is tolerably certain that neither of them is rigorously true, but it may be taken as proved that the heat liberated during the immersion of cotton is, for practical purposes, directly proportional to the weight of moisture absorbed. This does not necessarily mean that there is nothing else to be considered than the simple heat of liquefaction. It may be so, but the condensation of vapour may be supplemented by some other process, either exothermic or endothermic. The experimental method that has been employed cannot properly test the question thus raised, but the following rough calculation shows that there can be no very large difference between the heat of liquefaction and the heat of absorption by cotton :—

In Series V it was found that $k = 1{\cdot}1$ in the neighbourhood of the maximum temperature. Therefore, from the definition of k the heat capacity of the instrument used $= 1{\cdot}1x$, the heat liberated per milligramme of water absorbed. A measurement of the volume of the bulb and also of known lengths of the stem of the thermometer was made by weighing it suspended in water before it was covered with cotton, and the total volume of glass and mercury subsequently covered was calculated from these data to be 0·60 c.c. If the volume heats of glass and mercury be both taken as 0·45 cal. per c.c., which is not far from true, the heat capacity of that part of the thermometer which was directly affected was 0·27. The specific heat of cellulose is, according to Fleury,* 0·366, and as the cotton used weighed very nearly 0·900 gramme, the total heat capacity of the dry instrument may be taken as $0{\cdot}27 + 0{\cdot}33 = 0{\cdot}60$ cal. The addition for moisture already absorbed at the maximum temperature is about 0·03 cal. Hence, the heat evolved per milligramme of vapour absorbed is $\frac{0{\cdot}63}{1{\cdot}1} = 0{\cdot}57$ cal. This is practically equal to the heat liberated (0·576 cal.) when a milligramme of vapour at 25° condenses to form liquid water at 37°·7, which were the experimental conditions. But the uncertainties involved in the above calculation forbid any further conclusion than that already given, viz., that the heat of absorption by cotton is composed *mainly* of the heat of liquefaction of water.†

Summary and Discussion of Results.

In the preceding pages it has been shown (1) that the conspicuous rise of temperature which cotton undergoes when immersed in water and its subsequent slow fall follow the same course as the similar change which results from its exposure to air saturated with water vapour, and that both are affected in the same way by previous moisture and other conditions; (2) that in the latter case the heating is the direct result of the absorption of the vapour by the cotton, and that the two processes can be quantitatively connected; (3) that both absorption and heat production continue appreciably for many hours, though the rise of temperature is soon succeeded by a fall because the heating effect is counteracted by radiation, etc., and that the evidence points to no definite limit to the absorption process; (4) that the heat produced by the absorption is of about the same magnitude as the heat of liquefaction of the same quantity of water, but may be, in fact, either rather more or rather less; (5) that in the case of immersion in water, though the absorption of vapour cannot be observed, it must certainly occur, and that the air which adheres to each fibre and fills all interstices maintains that separation of water and cotton surfaces which is necessary for distillation to occur from one to the other.

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* 'Chem. Soc. Abstr.,' 1900, vol. 2, p. 188.

† The phenomena evidently have their origin in a difference of physical affinities, which implies *some* difference between their heats.

Two questions remain to be discussed, viz., the probable fate of the vapour after it has been condensed on the surface of the cotton, and the bearing of the conclusions here arrived at on the nature of the Pouillet effect in general.

As to the first question there seem to be three possible views. One of these—the view that it becomes chemically combined to form definite hydrates of cellulose—may be quickly dismissed, as there are no facts to support it and as the evidence points to the absence of any definite limit to the action. The ease with which the action is reversed (for the cotton parts with practically all its moisture if kept for a day at the ordinary temperature over sulphuric acid) is not by itself evidence against the chemical theory, but it may be mentioned here. At the opposite extreme is the view that the condensed moisture forms and remains as a liquid film on the surface of the solid. If it is so, the film must in time become a substantial one, as the following calculation shows.

The average diameter of cotton fibres varies, according to the quality, between 64×10^{-5} and 84×10^{-5} inch.* The mean of these may be taken as the most probable average diameter in the present case, viz., 74×10^{-5} inch, or 188×10^{-5} cm. Actual measurement of fibres under the microscope led to practically the same result but were not numerous enough to give a perfectly trustworthy average value. The density of cellulose may be taken as 1·525 (Clarke's Specific Gravity Table). The total surface of any given weight (w) of cotton may be calculated on the assumption that the fibres are uniform cylinders of such length that the ends are negligible, in which case the area is $4w/1{\cdot}525 \times 188 \times 10^{-5} = 1395w$ sq. cm. If m grammes of water be deposited on this surface as a film, the thickness of the film is $m/1395w$ sq. cm. In Experiment 20 of Series V (Table V) w was 0·90 gramme and m was shown to have attained the value 0·188 gramme at the end of 12 hours. In this case, therefore, the thickness of the film would be about 15×10^{-5} cm. Now Dr. G. J. Parks† concluded from similar calculations that in all such cases "the thickness of the surface film varies from 10×10^{-6} to 80×10^{-6} cm. according to the substances used and the conditions of temperature and pressure, and for the water film on glass in saturated vapour at 15° C. the thickness is about $13{\cdot}4 \times 10^{-6}$ cm." Hence the film on cotton in the above case was considerably outside Dr. Parks's superior limit, and it had by no means attained its full growth and, in fact, threatened to increase indefinitely.

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* Thorpe's 'Dict. of Techn. Chem.,' vol. 1, p. 613.

† "On the Thickness of the Liquid Film formed by Condensation at the Surface of a Solid," 'Phil. Mag.,' May, 1903, p. 517.

It seems probable, therefore, that the deposited moisture does not all remain as a mechanically adherent film on the surface of the cotton; and the third hypothesis may be suggested. This is, that it undergoes continuous osmotic diffusion into the substance of the fibre and forms with it what may be regarded as a solid solution of cellulose and water. Such a solution would exercise a vapour pressure of its own which would, at anything less than infinite dilution, be smaller than that of pure water at the same temperature. In a saturated atmosphere therefore equilibrium would never be reached, though the velocity of the absorption process would decrease continuously as the solution became more dilute. The heat developed locally by the action, *i.e.*, the heat due to the deposition of the liquid plus or minus a small heat of solution, would go to raise the temperature of the cotton above that of the neighbouring water by which the vapour is supplied, and would thus tend to check the action by increasing the vapour tension of the solution; but the natural cooling by radiation, etc., would again act as a counter-check. If placed in an atmosphere containing water vapour at anything less than saturation pressure (*e.g.*, in the open air) the cotton would, in time, reach a state of equilibrium either by absorption or by evaporation, according to its initial condition, and it would part with all its water if the surrounding atmosphere were maintained in a perfectly dry state, slowly or quickly according to the temperature. This is all in accordance with the ascertained facts, and as it is also inherently probable that the cotton fibre is permeable by water, the hypothesis appears to be justified.

As solids in general have the power of condensing vapours on their surface, it was not surprising to find a marked heat development on immersing cotton wool in air saturated with the vapour of absolute alcohol, gun-cotton in air saturated with water vapour, and glass wool in the same; but the effect was considerably smaller than when cotton wool was immersed in water vapour under similar conditions. In the case of glass wool the temperature curve was taken and weighings were made so as to determine the amount of vapour absorbed. The thermometer was wrapped as closely as possible with the material, which was secured by a few turns of fine aluminium wire, and the other arrangements were the same as in Series V. The glass wool weighed, after drying, 1·22 gramme. The diameter of the fibres was measured under the microscope and was found to vary from about 0·001—0·003 cm. It would have been necessary to make a large number of measurements to determine an accurate mean value, but 0·0025 cm. may be taken as near the mark; and this, with a density of 2·7, would make the total area of surface about 720 sq. cm. or about 0·57 of the area exposed by the cotton wool of Series V. The maximum rise was 1°·94 and 2°·1 in two experiments, and this was reached in 2 minutes, as nearly as possible. The first test was continued for 40 minutes, when about 17 milligrammes of vapour was found to have been condensed; the second was stopped at 5 minutes, when about 7 was the weight found. The temperature curve resembled that of cotton wool in a general way, for it rose steeply to the maximum and showed a slow descent; but its form was quite different in this, that it gave not even a rough approximation to those rules which have been found to govern the other case. This fact and the relatively small absorption (allowance being made for difference of surface area) are just what might be expected from the presumably impermeable character of glass, as here probably the condensed water remains as a mere surface film.

According to the views already put forward as to the cause of the temperature change when cotton is immersed in water itself, it seemed probable that little or no effect of the kind would be produced by immersing cotton in absolute alcohol or glass wool in water, though in both cases notable effects followed immersion in the bath of air saturated with vapour. As a fact, no change could be observed. In the case of glass wool and water, the test was very carefully carried out, and there was not the least sign of departure from the initial temperature, which was that of the thermostat surrounding the water. A change of 0°·02 could hardly have escaped notice. Apparently, then, the effect does not occur when the liquid is capable of rapidly and completely wetting the solid, and thus destroys the air insulation. In confirmation, it was found here, as in the case of "absorbent" cotton wool already described, that the thermometer when lifted from the bath carries with it a much larger weight of mechanically adhering water than comes away with a wrapping of cotton of the ordinary variety.

There is not the least doubt that the thermal effect dealt with in this paper is radically different from that investigated by Dr. G. J. Parks by the use of precipitated silica and of glass wool* and attributed by him to a pressure at the surface of contact of solid and liquid. In the first place, the Parks effect is manifested as a general rise of temperature on mixing the solid and water, and he detected it and determined its value by employing the immersion vessel as a calorimeter; whereas the cotton wool effect is essentially local and would be altogether prevented by any mixing process efficient enough to make complete contact between the solid and liquid. In the next place, Parks took the maximum temperature, reached in about 3 minutes, as indicative of the completion of the action, while it has been proved in the other case that the action, though leading to a maximum temperature in about the same time, has then but started on an apparently endless career. Finally Parks estimates the value of his heat production as about 0·001 cal. per sq. cm. of surface of exposed glass or silica, whereas it can be shown from facts already given that even in the case of saturated air immersion, about twelve times this quantity of heat is not generated but transferred per square centimetre of cotton wool in the first few minutes when, as just stated, only a small fraction of the total action has occurred. As the Parks effect is so small it is easy to understand how it escaped observation in the author's experiment with glass wool, already described, where the conditions were altogether unfavourable, having been arranged with a different object; for Parks himself, using a larger quantity of material, which he gently stirred with about the same amount of water as was contained in the author's immersion vessel, obtained a rise of only 0°·01.

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* 'Phil. Mag.,' August, 1902, p. 240, and May, 1903, p. 517.

It is difficult to say for certain whether the heating effects observed originally by Pouillet were due to the phenomenon investigated by Parks and styled by him "the Pouillet effect," or were the results of action similar to that described in this paper, or included both. But as he heaped his dry solid round the bulb of a delicate thermometer, and was careful not to disturb the heap by stirring it after adding the liquid, it is unlikely that true contact was established at once and completely, and it seems reasonable to suppose that he had to do with local heating by condensation of vapour. The still more striking, but similar observations of Martini* are probably to be explained in the same way and not, as he suggests, by the solidification of liquid water.

In conclusion, it may be pointed out that the hygroscopic behaviour of cellulose and the thermal changes associated with it have a practical importance of their own on the side of vegetable physiology, and perhaps also in other directions, apart from any interest they may have on purely physical grounds.

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* 'Phil. Mag.' [5] vol. 47, p. 329; vol. 50, p. 618; [6] vol. 5, p. 595.

"Enhanced Lines of Titanium, Iron, and Chromium in the Fraunhoferic Spectrum." By Sir J. Norman Lockyer, K.C.B., LL.D., F.R.S., and F. E. Baxandall, A.R.C.S. Received July 13, 1904.

In previous publications it has been shown that the enhanced lines of some of the metals are prominent in the spectra of α Cygni* and the sun's chromosphere†, while it is generally recognised that the lines in the Fraunhoferic spectrum are mainly the equivalents of lines in the arc spectra of metals. In connection with the work on enhanced lines, it has been noted that some of them, at least, appear to correspond with comparatively weak solar lines to which Rowland has attached no origin. With the object of possibly tracing some of the unorigined solar lines to their source, a careful comparison has been made between the enhanced lines shown in the photographic spark spectra of titanium, iron, and chromium, and the solar lines. The photographs used for this purpose were all taken with a Rowland grating, under exactly similar conditions, and on such a scale that the length of spectrum between K and F is about 14 inches (35 cms.). The chemical elements named were first selected for investigation because they furnish by far the greater number of enhanced lines which have been shown to occur in the spectrum of α Cygni. It was an easy matter, owing to the many solar coincidences with lines of these elements, to adjust the compared photographs and get the spectrum lines in proper alignment.

It was found that many of the enhanced lines fell exactly and squarely on isolated lines of the solar spectrum, and in these cases the solar wave-lengths were adopted, and the identification considered established. If, however, for any of these solar lines Rowland had given alternative origins, special comparisons were made of the enhanced line photograph and those of the metals given by Rowland. Notes were made as to the agreement or non-agreement of the metallic lines involved, and also of the relative intensities in their individual spectra, so that due weights could be given to the respective metallic lines which were thought to conjointly produce compound solar lines.

Where there was any doubt as to the exact coincidence of a metallic and solar line, or where by the close grouping of several solar lines it was not possible to say by direct comparison to which solar line the metallic line corresponded, careful measures were made of the metallic line, and its wave-length found by interpolation between closely adjacent lines of known wave-length. The resulting wave-lengths were then compared with Rowland's solar wave-lengths, and in cases of close agreement with solar lines it was deemed probable that the two lines were really identical. In this connection, however, the relative intensities of the solar and enhanced lines were, to a great extent, taken into account in judging whether a solar line could be accepted as the analogue of a metallic line.

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* 'Roy. Soc. Proc.,' vol. 64, p. 321.

† 'Roy. Soc. Proc.,' vol. 68, p. 178.

The three elements investigated are dealt with separately. The tables show the wave-lengths of the enhanced lines as reduced from the most recent and best photographs, their intensities in spark and arc spectra, the wave-lengths of Rowland's solar lines to which they probably correspond, and the origins, if any, to which Rowland has attributed such solar lines.

The wave-lengths of some of the enhanced lines differ in the second decimal place from those published* previously for the same lines. More weight can be given to the present wave-lengths, as in the photographs from which they have been reduced the lines are more sharply defined than in the earlier photographs employed. In the case of chromium a much more extended list of enhanced lines than the previous one has been obtained.

The numbers in the last column refer to the notes at the end of each table.

Titanium.

λ. Enhanced Ti lines.	Intensity.		Fraunhoferic lines (Rowland).		Rowland's origin.	Notes appended.
	Spark, max. 10.	Arc, max. 10.	λ.	Int., max. 1000.		
3813·54	4	1—2	3813·54	2	C	1
3814·72	5	2—3	3814·74	3	C	2
3836·23	4	1—2	3836·23	2	—	3
3900·68	10	4	3900·68	5	Ti-Fe-Zr	[1]
3913·61	10	4	3913·61	5	Ti-Fe	[2]
3932·16	4	trace	3932·16	1	Ti	
3987·75	1	0	3987·76	2	Ti ?	
4012·54	5	1	4012·54	4	Ti	
4025·29	3	1	4025·29	3	Ti	
4028·50	6	1	4028·50	4	Ti	
4053·98	5	trace	4053·98	3	Fe-Ti	[3]
4055·19	2	1	4055·19	3	Ti-Fe	[4]
4161·70	2—3	0	4161·68	4	—	4
4163·82	10	2	4163·82	4	Ti, Cr	[5]
4172·07	10	1	4172·07	2	Ti-Fe	[6]
4173·70	3	0	4173·71	3	—	[7]
4174·20	2	0	4174·24	0	—	
4184·49	1	0	4184·47	2	—	[8]

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* 'Roy. Soc. Proc.,' vol. 65, p. 451.

Titanium—*continued.*

λ. Enhanced Ti lines.	Intensity.		Fraunhoferic lines (Rowland).		Rowland's origin.	Notes appended.
	Spark, max. 10.	Arc, max. 10.	λ.	Int. max. 1000.		
4227 ·46	2	0	4227 ·47	1	—	5
4290 ·38	6	2	4290 ·38	2	Ti	
4294 ·20	7	3	4294 ·20	2	Ti	
4300 ·21	6	1—2	4300 ·21	3	Ti	
4302 ·09	3	1—2	4302 ·09	2	Ti	
4308 ·06	7	1—2	4308 ·08	6	Fe	6
4313 ·03	7	1—2	4313 ·03	3	Ti	
4315 ·14	8	1	4315 ·14	3	Ti	
4316 ·96	2	0	4316 ·96	1	Ti ?	
4321 ·12	3	1	4321 ·12	2	—	
4330 ·40	2	trace	4330 ·41	1	—	
4330 ·87	2	trace	4330 ·87	2	Ti-Ni	[9]
4338 ·08	8	4	4338 ·08	4	Ti	
4341 ·53	3	1	4341 ·53	2	Ti ?	
4374 ·96	3	0	4374 ·98	0	Zr	[10]
4387 ·01	5	trace	4387 ·01	1	Ti ?	
4391 ·19	1—2	trace	4391 ·19	1	Ti	
4395 ·20	9	5	4395 ·20	3	Ti	
4396 ·01	2	trace	4396 ·01	1	Ti	
4399 ·94	7	3	4399 ·94	3	Ti-Cr	[11]
4411 ·24	5	trace	4411 ·24	1	Cr	[12]
4417 ·88	6	2	4417 ·88	3	Ti	
4421 ·93	3	2	4421 ·93	00	Ti	
4443 ·98	9	4	4443 ·98	5	Ti	
4450 ·65	3	1	4450 ·65	2	Ti ?	7
4464 ·62	3	1	4464 ·62	2	Ti ?	8
4468 ·66	9	4	4468 ·66	5	Ti	
4488 ·49	5	1	4488 ·49	1	—	
4501 ·45	8	4	4501 ·45	5	Ti	
4529 ·69	3	trace {	4529 ·66	1	—	[13]
			4529 ·73	1	.....	
4534 ·14	5	2	4534 ·14	6	Ti-Co	[14]
4549 ·81	8	4	4549 ·81	6	Ti-Co	[15]
4563 ·94	7	3	4563 ·94	4	Ti	
4572 ·16	9	4	4572 ·16	6	Ti	
4590 ·13	3	1—2	4590 ·13	3	—	
4657 ·38	2	trace	4657 ·38	2	Ti ?	
4764 ·10	1	0	4764 ·11	4	Ti-Ni	[16]

1. Ti probably true origin.
2. Ti probably true origin.
3. Ti line and solar line exactly coincident.
4. Solar line possibly only partially due to Ti.
5. Solar line exactly coincident with *p* Ti line.
6. This *p* Ti line is apparently exactly coincident with the Fe line, and solar line is probably compounded of both.
7. Solar line doubtless due to Ti.
8. Solar line doubtless due to Ti.

Notes on *p* Ti-Solar Lines.

(The figures at the head of each note refer to Rowland's solar lines.)

[1.] **3900·68 (5), Ti-Fe-Zr.—The titanium line involved in the solar line is one of the very strongest in the spark spectrum.** The iron line is only a weak one, and, in the light of other adjacent iron lines of equal intensity, would of itself only produce a solar line of intensity 2 or 3. In apportioning the weights to the various elements, which possibly take part in the formation of the solar line, zirconium can be almost ignored. There are many far stronger lines of zirconium than the one in question which are not represented in the sun at all. It would appear, then, that the solar line 3900·68 is really made up of the *p* Ti and Fe lines in about equal proportions.

[2.] 3913·61 (5), Ti-Fe.—It is very doubtful whether Fe takes any part in the production of this solar line. There is no such iron line recorded by either Kayser and Runge or Exner and Haschek, and there is no trace of a line in any of the Kensington photographs. The titanium line is a very prominent one in the spark spectrum, and quite capable of producing the solar line of itself.

[3.] 4053·98 (3), Fe-Ti.—The iron line is an extremely faint one, while the titanium line is well marked. The solar line is probably a composite one, but more attributable to titanium than iron.

[4.] 4055·19 (3), Ti-Fe.—The iron and titanium lines are coincident, and about equally strong. Solar line probably due to both.

[5.] 4163·82 (4), Ti-Cr.—Both the titanium and chromium lines are well marked in their respective spectra. The former seems to be slightly less refrangible than the other. The solar line is probably a very close double, and due to both Ti and Cr.

[6.] 4172·07 (2), Ti-Fe.—The iron line is extremely weak, while the *p* Ti line is one of the strongest in the spectrum. The solar line is probably due chiefly to Ti.

[7.] 4173·71 (1); no origin by Rowland.—The mean result of two measurements of this enhanced titanium line gives λ 4173·71. Its identity with the solar line is therefore well established.

[8.] 4184·47 (2); no origin by Rowland.—The published wave-length of this enhanced titanium line was 4184·40. A re-estimation from a later grating photograph gives as a resulting wave-length 4184·49. There is little doubt of its identity with the solar line 4184·47.

[9.] 4330·87 (2), Ti-Ni.—The nickel line is an exceedingly weak one, and it is doubtful whether the solar line is partially produced by it. Rowland, in a footnote in his 'Tables of Solar Wave-Lengths,' says: "This is a weak, hazy, nickel line. It is on the red edge of the solar line, and the Ti line is nearer the centre."

[10.] 4374·98 (0), Zr.—The published wave-length of the enhanced titanium line was 4374·90. A re-estimation from a better photograph gives 4374·99. It is probably identical with the weak solar line 4374·98, which Rowland ascribes to Zr.

[11.] 4399·94 (3), Ti-Cr.—The chromium line, although apparently coincident with the titanium and solar lines, is a very weak one. On the other hand, the titanium line is quite well marked. The solar line is therefore probably due chiefly to titanium.

[12.] 4411·24 (1), Cr.—Re-measurement of the proto-titanium line gives λ 4411·24. It is apparently coincident both with the chromium and solar lines. The chromium line is a weak one, whereas the titanium line is well marked, and there is little doubt that the solar line is partially, if not chiefly, due to titanium.

[13.] $\left.\begin{array}{l}4529{\cdot}66\ (1)\\ 4529{\cdot}73\ (1)\end{array}\right\}$ No origin by Rowland.—The published wave-length of the enhanced titanium line was 4529·60. Re-measurement from the latest grating photograph gives λ 4529·69. It is doubtful which of the two solar lines, 4529·66, 4529·73, the titanium line represents. It is quite possible that the latter is a very close double, and may account for both solar lines.

[14.] 4534·14 (6), Ti-Co.—Both the titanium and cobalt lines are well marked in their respective spectra, and there is little doubt that the solar line is compounded of the two.

[15.] 4549·81 (6), Ti-Co.—The titanium and cobalt lines are apparently coincident, and as each is a strong line in its own spectrum, the solar line is probably compounded of both in about equal proportion.

[16.] 4764·11 (4), Ti-Ni.—The enhanced titanium line is a very weak one, and the probability is that Ni is the chief origin of the solar line.

Iron.

λ. Enhanced Fe lines.	Intensity.		Fraunhoferic lines (Rowland).			Notes appended.
	Spark, max. 10.	Arc. max. 10.	λ.	Int., max. 1000.	Origin.	
3839·78	2—3	0	3839·76	2	Fe	
3846·55	2—3	1	3846·55	2	Fe	
3863·87	3	1—2	3863·89	3	Fe	
3871·86	4	1—2	3871·96	2	Fe	
3906·14	1	0	3906·17	00	—	
3935·92	5	4	3935·97	2	Fe	
3939·28	1—2	0	3939·29	0	—	
4002·77	1—2	trace	4002·81	0	—	
4048·93	3—4	2	4048·91	5	Mn-Cr	1
4055·73	3	2	4055·70	6	Mn	2
4173·61	3	1—2	4173·62	3	—	
4179·05	3—4	trace	4179·03	3	—	
4233·32	4—5	0	4233·33	4	Mn-Fe	[1]
4296·72	2	0	4296·74	3	—	
4302·35	2—3	2	4302·35	2	Fe	
4303·34	3—4	0	4303·34	2	—	
4351·93	5	0	4351·93	5	Cr	[2]
4385·55	3—4	trace	4385·55	2	—	
4451·75	3	2	4451·75	3	Mn	3
4462·30	2	0	—	—	—	4
4489·35	1	0	4489·35	2	—	
4491·57	2	0	4491·57	2	—	
4508·46	5	trace	4508·46	4	Fe ?	
4515·51	4	trace	4515·51	3	—	
4520·40	3	1	4520·40	3	Fe ?	
4522·77	6	2	4522·81	0	—	5
4541·46	3	1	4541·48	0	—	
4549·64	7	1	4549·64	2	Fe	
4556·09	5	0	4556·06	3	—	
4576·51		0	4576·51	2	—	
4584·02	8	1	4584·02	4	Fe	
4629·51	4	0	4629·52	6	Ti-Co	[3]
4635·50	8	0	4635·49	0	—	
4924·11	8	0	4924·11	5	Fe	
5018·63	7	1	5018·63	4	Fe	
5169·07 5169·22	6	2	5169·07 5169·22	3 4	Fe Fe	
5276·17	2	0	5276·17	3	Fe ?	
5316·79	8	0	5316·79	4	Fe	

1. Probably partly due to the enhanced Fe line, in addition to Mn and Cr.
2. Solar line probably due partly to *p* Fe. K and R's λ 4055·63 (4).
3. Solar line probably compounded of the *p* Fe and Mn lines.
4. The *p* Fe line is apparently slightly more refrangible than solar line 4462·37.
5. This *p* Fe line is probably identical with Rowland's solar line 4522·81 rather than with 4522·69, to which he gives a Fe? origin.

Notes on Certain *p* Fe-Solar Lines.

[1.] λ 4233·33 (4).—This solar line was ascribed by Rowland to Mn-Fe in his "Preliminary Table of Solar Wave-lengths." In the revised table[*] the Fe origin is discarded and the sole origin given as Mn. There appears to be, however, no evidence for the line being due to manganese. There is no trace whatever of a line in this position in any of the Kensington photographs of the manganese spectrum, and no such line is given by Hasselberg[†] in his comprehensive list of manganese arc lines. Although the arc line of iron at the corresponding wavelength is exceedingly weak—in many photographs it does not occur at all—there is no doubt about there being a prominent line in the spark spectrum. The solar line in question is probably due solely to iron, and is the counterpart of the enhanced line of that metal. In *α* Cygni the line 4233·33 is quite an outstanding line and one of the very strongest in the spectrum.

[2.] 4351·93 (5), Cr.—This solar line is ascribed by Rowland solely to Cr. Although the chromium line is a moderately strong one it is scarcely likely that its solar equivalent would be as strong as that of the chromium line 4289·89, one of the very strongest lines in the spectrum of that element. The two solar lines mentioned being, however, of the same intensity, in all probability that at λ 4351·93 is partially due to some other element. The strongly enhanced Fe line 4351·93 is apparently exactly coincident with the Cr line, and as other similarly enhanced Fe lines occur amongst the Fraunhoferic lines it is probable that the solar line in question is compounded of the iron and chromium lines.

In *α* Cygni there is a corresponding well-marked line which, in the light of the complete absence from the stellar spectrum of chromium arc lines, can only be attributed to proto-iron. This is the more likely as the other enhanced lines of iron are so prominent in the *α* Cygni spectrum.

This line in stellar spectra has been attributed by Scheiner to the magnesium arc line 4352·08 and on its behaviour with respect to the stellar representative of the characteristic spark line of magnesium 4481·3, he has based conclusions[‡] on the relative temperatures of the absorbing atmospheres of various stars. Such conclusions are not trustworthy, as the origin of the line is obviously not the same in all stellar spectra. In stars of the solar type the line is probably of a complex origin, Cr 4351·93, Mg 4352·08, and *p* Fe 4351·93, all being involved. In higher temperatures stars like *α* Cygni, Sirius, and Rigel there is abundant evidence in favour of a proto-Fe origin and little or none for either chromium or magnesium. Thus, other lines of Cr and Mg, which are similar in intensity and behaviour in their respective spectra to those mentioned above, are all unrepresented in these stellar spectra, whereas all the enhanced Fe lines of similar intensity and behaviour to the line 4351·93 are strongly represented in the same stellar spectra.

[3.] 4629·52 (6), Ti-Co.—It is doubtful whether the Ti and Co lines are collectively strong enough to account for the intensity of the solar line. The equally strong Co line 4663·59 only furnishes a solar line of intensity 0, and the stronger

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[*] 'Ast. Phys. Jour.,' vol. 6, p. 384, 1897.

[†] 'Kongl. Sv. Vet. Akademiens Handlingar,' Bd. 30, No. 2.

[‡] 'Ast. and Ast. Phys.,' vol. 13, p. 569.

Ti line 4623·28 corresponds to a solar line of intensity 2. It is scarcely likely, then, that the superposition of the Ti and Co lines at 4629·60 would produce a solar line of intensity 6. The proto-iron line at the same wave-length probably supplies the deficiency in intensity. The enhanced line of iron 4515·51, which is of about equal prominence as 4629·60, has an equivalent solar line of intensity 3, and if the *p* Fe line 4629·60 of itself produces a similar solar line, then the intensity 6 of the solar 4629·60 could be easily accounted for. In fact, it is quite probable that the solar line in question is built up of the lines at the same wave-length belonging to Ti, Co, and *p* Fe, and that the proto-iron line has, if anything, the greatest share in its production.

There is a fairly good corresponding line in the chromospheric spectrum, and, in the publication of eclipse results by various observers, the origin of the line is invariably given as Ti-Co, presumably because they have established its identity with the Fraunhoferic line and accepted Rowland's origin as a correct and sufficient one. In the chromosphere it is probably chiefly due to *p* Fe, as the ordinary Ti and Co lines are there only weak, while the enhanced iron lines are well marked. There is also a corresponding line in the spectrum of α Cygni. Here, however, the origin is evidently proto-iron only, as the arc lines of cobalt and titanium are entirely missing from the stellar spectrum; whereas nearly all the proto-iron lines are well seen.

Chromium.

λ. Enhanced Cr lines.	Intensity.		Fraunhoferic lines (Rowland).		Rowland's origin.	Notes appended.
	Spark, max. 10.	Arc, max. 10.	λ.	Int., max. 1000.		
3814 ·07	2	0	3814 ·07	1	—	
3865 ·67	7	<1	3865 ·67	7	Fe-Cr	1
3866 ·69	1—2	0	—	—	—	
3905 ·66	6	0	3905 ·66	12	Si	2
3979 ·66	5—6	0	3979 ·66	4	Co	[1]
4003 ·55	4	0	—	—	—	
4012 ·63	6—7	2	4012 ·63	0	Cr	
4038 ·10	4—5	0	—	—	—	
4052 ·10	3	0	4052 ·18	0	—	
4058 ·92	5	3—4	4058 ·92	3	Fe-Cr	3
4071 ·07	4	0	4071 ·14	00	—	
4082 ·50	2—3	0	4082 ·43	0	—	
4111 ·25	4	0	—	—	—	
4145 ·91	6	0	4145 ·91	1	—	
4225 ·02	4	0	4225 ·02	2	—	
4233 ·50	2—3	0	—	—	—	
4242 ·54	6—7	0	4242 ·54	2	—	
4252 ·80	3	0	4252 ·79	0	—	
4262 ·15	5	0	4262 ·09	1	—	4
			4262 ·14	1	—	
4269 ·41	2	0	4269 ·45	0	—	
4284 ·38	3—4	0	4284 ·38	2	—	5
4307 ·20	2—3	0	—	—	—	
4555 ·16	5—6	1	4555 ·16	2	—	
4558 ·83	10	1	4558 ·83	3	Cr ?	
4588 ·38	10	1	4588 ·38	3	—	

Chromium—*continued.*

λ. Enhanced Cr lines.	Intensity.		Fraunhoferic lines (Rowland).		Rowland's origin.	Notes appended.
	Spark, max. 10.	Arc, max. 10.	λ.	Int., max. 1000.		
4592·23	4—5	0	4592·23	1	Cr	
4616·80	3—4	0	4616·80	1	—	
4618·97	8	0	4618·97	4	Fe	[2]
4684·25	8	0	4634·25	2	—	
4812·72	2—3	0	—	—	—	
4824·33	8	0	4824·33	3	Fe	6
4836·40	2—3	0	4836·42	0	—	
4848·44	6	0	4848·44	2	—	
4856·37	1	0	—	—	—	
4864·51	5	0	4864·51	1	—	
4876·59	5	0	4876·59	1	—	

1. Fe line and *p* Cr lines apparently coincident. Solar line probably compounded of both.
2. *p* Cr and Si lines exactly coincident. Solar line probably due to both, but mostly to Si.
3. Solar line probably due more to *p* Cr than Fe.
4. *p* Cr line possibly double.
5. Solar line possibly due partly to some other element.
6 Solar line probably compounded of Fe and *p* Cr lines.

Notes on Certain *p* Cr-Solar Lines.

[1.] λ 3979·66, Co (4).—This enhanced line of chromium is apparently coincident with a cobalt line, and also with the solar line λ 3979·664, to which Rowland assigns a cobalt origin. As the adjacent cobalt line 3958·07 is quite as strong as 3979·66, and only furnishes a solar line of intensity 2, it is not probable that the solar line corresponding to 3979·66 would be of intensity 4, unless a line of some other element were involved. It is very probable that the solar line in question is compounded of the *p* Cr and Co lines.

[2.] λ 4618·97, Fe (4).—This strongly enhanced Cr line is apparently coincident with the solar line 4618·97 (intensity 4), Rowland's origin for which is Fe. The nearest line of iron to this in Kayser and Runge's list is 4618·88 (2). Assuming that this is identical in position with the solar line, its intensity is far too low to account for the solar intensity. The closely adjacent iron line 4619·40, which is of intensity 6, gives a solar line of intensity 3, so that it is very improbable that the far weaker iron line 4618·21 will produce a solar line of intensity 4. There is little doubt that the solar line 4618·97 is chiefly accounted for by the strongly enhanced chromium line, but the iron line at the same position probably adds slightly to the solar intensity.

FRAUNHOFERIC LINES DUE TO *p* Ti, *p* Fe, or *p* Cr.

The following table contains the Fraunhoferic lines which are, as a result of the present discussion, considered to be due, either wholly or partially, to enhanced lines of titanium, iron, or chromium. Rowland's wave-lengths have been adopted with the modification that the last figure in the decimals has been dropped, and the numbers given to the nearest second decimal. In such an inquiry as the present one, this can be done without affecting the validity of the results. In the first place, the spark lines are generally of a wider and hazier nature than the arc lines, and consequently their wave-lengths cannot be estimated to as great a degree of accuracy. Again, the conclusions as to the identity of the solar and enhanced lines are not based on one or two coincidences only, but on the apparent agreement of a whole series of lines for each element.

It will be seen that some forty-two lines which were unorigined by Rowland are here attributed to proto-titanium, proto-iron, or proto-chromium. Compared with the host of lines in Rowland's tables this may seem a very insignificant number, but the importance of establishing their origins does not lie in their number, but in the fact that they are lines of a special nature, and just those metallic lines which are prevalent in the spectra of the higher temperature stars, such as α Cygni and Sirius, to the exclusion of the great majority of the other solar lines.

The enhanced lines have previously been identified with stellar lines, which in such stars as α Cygni, Sirius, and Rigel are of a more isolated nature than in the solar spectrum, and if the same lines can be established as occurring in the solar spectrum it at once standardises the wave-lengths of many stellar lines, and will thus be of importance in any stellar inquiry in which it is necessary to have accurate wave-lengths for the spectral lines.

In some cases it has been found that there is no justification for the origin given by Rowland. These, however, are very few, and are indicated in the notes appended.

In others, Rowland's origin does not appear to be a sufficient one, that is, the intensity of the solar lines cannot be adequately accounted for by the lines of the elements to which he ascribes them. In such cases it is probable that the solar lines are due partly to the arc lines of the elements quoted by Rowland and partly to the enhanced lines of either Fe, Ti, or Cr, which occur at or very near the same wave-lengths.

A glance at the table will show that for many lines the same element is given in the two columns for origins, the Kensington origin having the prefix "p." This simply means that there is an enhanced line of that particular element at the given wave-length, which is not entirely absent from the arc spectrum, and that Rowland has identified the solar line with the arc equivalent of the enhanced line. Seeing, however, that most of these lines occur in stellar spectra, where hosts of stronger arc lines are missing; it will, perhaps, be more appropriate to designate them as of a proto-metallic origin even in the sun.

Solar Lines due either wholly or partially to Enhanced Lines of Ti, Fe, or Cr.

Fraunhoferic lines (Rowland).			Probable origin (Kensington).	Notes appended.
λ.	Int., max. 1000.	Origin.		
3813·54	2	C	*p* Ti	
3814·74	3	C	*p* Ti	
3836·23	2	—	*p* Ti	
3839·76	2	Fe	*p* Fe	
3846·55	2	Fe	*p* Fe	
3863·89	3	Fe	*p* Fe	
3865·67	7	Fe-C	Fe-*p* Cr	
3871·96	2	Fe	*p* Fe	
3900·68	5	Ti-Fe-Zr	*p* Ti-Fe	1
3905·66	12	Si	Si *p* Cr	
3906·17	00	—	*p* Fe	
3918·61	5	Ti-Fe	*p* Ti	2
3932·16	1	Ti	*p* Ti	
3935·97	2	Fe	*p* Fe	
3939·29	0	—	*p* Fe	
3979·66	4	Co	Co *p* Cr	
3987·76	2	Ti ?	*p* Ti	
4002·81	0	—	*p* Fe	
4012·54	4	Ti	*p* Ti	
4012·68	0	Cr	*p* Cr	
4025·29	3	Ti	*p* Ti	
4028·50	4	Ti	*p* Ti	
4048·91	5	Mn-Cr	Mn-Cr-*p* Fe	3
4053·98	3	Fe-Ti	*p* Ti-Fe	
4055·19	5	Ti-Fe	*p* Ti, Fe	
4055·70	6	Mn	Mn *p* Fe	4
4058·92	3	Fe-Cr	Cr *p* Fe	5
4145·91	1	—	*p* Cr	
4161·68	4	—	*p* Ti	6
4163·82	4	Ti-Cr	*p* Ti, Cr	
4172·07	2	Ti-Fe	*p* Ti	7
4173·62	3	—	*p* Fe	
4173·71	3	—	*p* Ti	
4174·24	0	—	*p* Ti	
4179·03	3	—	*p* Fe	
4184·47	2	—	*p* Ti	
4225·02	2	—	*p* Cr	
4227·47	1	—	*p* Ti	
4233·33	4	Mn	*p* Fe	8
4242·54	2	—	*p* Cr	
4252·79	0	—	*p* Cr	
4262·09	1	—	*p* Cr	9
4262·14	1	—		

Solar Lines due to Enhanced Lines of Ti, Fe, or Cr—*continued.*

Fraunhoferic lines (Rowland).			Probable origin (Kensington).	Notes appended.
λ*	Int., max. 1000.	Origin.		
4284 ·38	2	—	*p* Cr	
4290 ·38	2	Ti	*p* Ti	
4294 ·20	2	Ti	*p* Ti	
4296 ·74	3	—	*p* Fe	
4300 ·21	3	Ti	*p* Ti	
4302 ·09	2	Ti	*p* Ti	
4302 ·35	2	Fe	*p* Fe	
4303 ·34	2	—	*p* Fe	
4308 ·08	6	Fe	Fe *p* Ti	
4313 ·03	3	Ti	*p* Ti	
4315 ·14	3	Ti	*p* Ti	
4316 ·96	1	Ti ?	*p* Ti	
4321 ·12	2	—	*p* Ti	
4330 ·41	1	—	*p* Ti	
4330 ·87	2	Ti-Ni	*p* Ti	10
4338 ·08	4	Ti	*p* Ti	
4341 ·53	2	Ti ?	*p* Ti	
4344 ·45	2	Ti	*p* Ti	
4351 ·00	1	Ti	*p* Ti	
4351 ·93	5	Cr	Cr *p* Fe	
4367 ·84	2	Ti	*p* Ti	
4374 ·98	0	Zr	*p* Ti	11
4385 ·55	2	—	*p* Fe	
4387 ·01	1	Ti ?	*p* Ti	
4391 ·19	1	Ti	*p* Ti	
4395 ·20	3	Ti	*p* Ti	
4396 ·01	1	Ti	*p* Ti	
4399 ·94	3	Ti-Cr	*p* Ti Cr	12
4411 ·24	1	Cr	*p* Ti Cr	
4417 ·88	3	Ti	*p* Ti	
4421 ·93	00	Ti	*p* Ti	
4443 ·98	5	Ti	*p* Ti	
4450 ·65	2	Ti ?	*p* Ti	
4451 ·75	3	Mn	Mn *p* Fe	
4464 ·62	2	Ti ?	*p* Ti	
4468 ·66	5	Ti	*p* Ti	
4488 ·49	1	—	*p* Ti	
4489 ·35	2	—	*p* Fe	
4491 ·57	2	—	*p* Fe	
4501 ·45	5	Ti	*p* Ti	
4508 ·46	4	Fe ?	*p* Fe	
4515 ·51	3	—	*p* Fe	
4520 ·40	3	Fe ?	*p* Fe	
4522 ·81	3	—	*p* Fe	
4529 ·66 }	1	—	} *p* Ti	13
4529 ·73 }	1	—		
4534 ·14	6	Ti-Co	*p* Ti-Co	
4541 ·48	0	—	*p* Fe	
4549 ·64	2	Fe	*p* Fe	
4549 ·81	6	Ti-Co	*p* Ti, Co	
4555 ·16	2	—	*p* Cr	
4556 ·06	3	—	*p* Fe	
4558 ·83	3	Cr ?	*p* Cr	

Solar Lines due to Enhanced Lines of Ti, Fe, and Cr—*continued.*

Fraunhoferic lines (Rowland).			Probable origin (Kensington).	Notes appended.
λ.	Int., max. 1000.	Origin.		
4563·94	4	Ti	*p* Ti	
4572·16	6	Ti	*p* Ti	
4576·51	2	—	*p* Fe	
4584·02	4	Fe	*p* Fe	
4588·38	3	—	*p* Cr	
4590·13	3	—	*p* Ti	
4592·25	1	Cr	*p* Cr	
4616·81	1	—	*p* Cr	
4618·97	4	Fe	*p* Cr-Fe	14
4629·52	6	Ti Co	*p* Fe, Ti, Co	
4634·25	2	—	*p* Cr	
4635·49	0	—	*p* Fe	
4657·38	2	Ti ?	*p* Ti	
4824·33	3	Fe	Fe *p* Cr	
4836·42	0	—	*p* Cr	
4848·44	2	—	*p* Cr	
4864·51	1	—	*p* Cr	
4876·59	1	—	*p* Cr	

1. Zr negligible.
2. No evidence for Fe origin.
3. Chiefly due to Mn.
4. Chiefly due to Mn.
5. Chiefly due to *p* Cr.
6. Possibly due partially to some other element.
7. No evidence for Fe origin.
8. No evidence for Mn.
9. Doubtful which is really due to *p* Cr.
10. Evidence for Ni doubtful.
11. No evidence for Zr.
12. Chiefly due to *p* Ti.
13. Doubtful which is really due to *p* Ti.
14. Chiefly due to *p* Cr.

GENERAL CONCLUSIONS.

As a general summary of the results of the foregoing analysis it may be stated :—

1. The enhanced lines of titanium and iron are practically all represented in the Fraunhoferic spectrum, but in some cases the corresponding solar lines are compound, and only partly due to one or other of these metals.

2. The corresponding solar lines are, generally speaking, comparatively weak ones.

3. The majority of the chromium enhanced lines occur in the solar spectrum, though some appear to be missing.

4. Some of the Fraunhoferic lines correspond to metallic lines special to the spark spectrum, and lacking in the arc, and probably for this reason they were left unorigined by Rowland.

"Air Resistance Encountered by Projectiles at Velocities up to 4500 Feet per Second." By A. Mallock, F.R.S. Received November 3,—Read November 17, 1904.

The work done by Prof. Bashforth on the subject of air resistance is so well known that I need hardly refer to it except to say that his results have, with minor alterations, been confirmed by subsequent experimenters. The greater part of Professor Bashforth's work related to velocities under 2500 feet per second, and the object of the present experiments was to examine the co-efficient of air resistance at higher speeds.

In the years 1895–97, Major the Hon. T. F. Fremantle and Colonel H. Mellish made a series of experiments on the remaining velocities of the service ·303 bullet by shooting into a ballistic pendulum from ranges varying from 12 up to 1000 yards. These experiments were made with great care, each bullet and charge being separately weighed, and from the results which they communicated to me I computed the co-efficient of resistance for velocities ranging from 2100 f.s. to 900 f.s. I suggested then that with light bullets we could probably extend the ballistic tables very considerably, using the pendulum to measure the velocity, and shortly after this we made some trials with various aluminium bullets. We found, however, that with cordite of the size used for the service charge of the ·303 rifle a great part of the explosive was blown out unburnt when the light bullets were used. It was evident, therefore, that in order to get the velocities we required, a much finer cordite than the No. 3 of the service charge would have to be used. We found also that a considerable deposit of aluminium was left in the barrel after firing.

From various causes I have not been able to proceed with the experiments until the present year, when having obtained some cordite of diameter ·01 inch, I again tried aluminium bullets, but the metallic fouling proved fatal to accurate and consistent results. I then tried shooting with lignum vitæ plugs which did very well up to velocities of about 2500 f.s., but at this velocity, sometimes, and generally at higher velocities, the plugs broke up under the action of centrifugal force. I again, therefore, reverted to aluminium, but on the bullets I made two small cannelures, fig. 1, which were filled with a composition of equal parts of black lead and tallow. These bullets answered admirably, and in July of the year I completed a series of experiments going up to velocities of 4500 f.s.

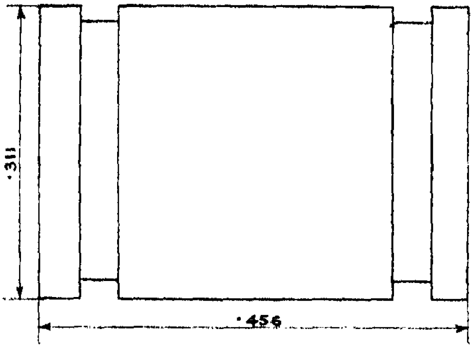

FIG. 1.—Aluminium shot used in air-resistance experiments. Scale five times actual size. Weight 23·3 grains.

The results of these experiments are given in the figs. 2 and 3, together with the results obtained from the shooting by Major Fremantle and Colonel Mellish, with the service bullet, and also, for comparison, Professor Bashforth's results.

Curve A, fig. 2, gives the velocities in feet per second, found at various ranges, and curve B, the loss of velocity in a distance of 5 yards. (It may be noted that at 4500 f.s. the retardation experienced by the light shot used was 205000 feet per second per second.) Curve A, fig. 3, gives the deduced resistance (in lbs. per square inch), encountered by the projectile, in terms of velocity.

To determine the resistance of an ogival-headed shot from the resistance experienced by a flat-headed shot moving with the same velocity, the resistance of the latter must be multiplied by a co-efficient, which is generally taken as $\frac{1}{2}$.

If the circular edges of the flat head are slightly rounded this value is nearly correct, but I have found by experiment that when the edges of the flat are quite sharp (as they were with the aluminium cylinders used), the co-efficient is rather less than half.*

In curve B, fig. 3, the co-efficient was taken as $\frac{1}{2\cdot1}$, and this curve represents, at any rate, very approximately, the resistance experienced by an ogival-headed shot. Curves C and D, fig. 3, give respectively, the results obtained from the experiments of Major Fremantle and Colonel Mellish, made with the ·303 rifle, and by Professor Bashforth from his experiments with large guns.

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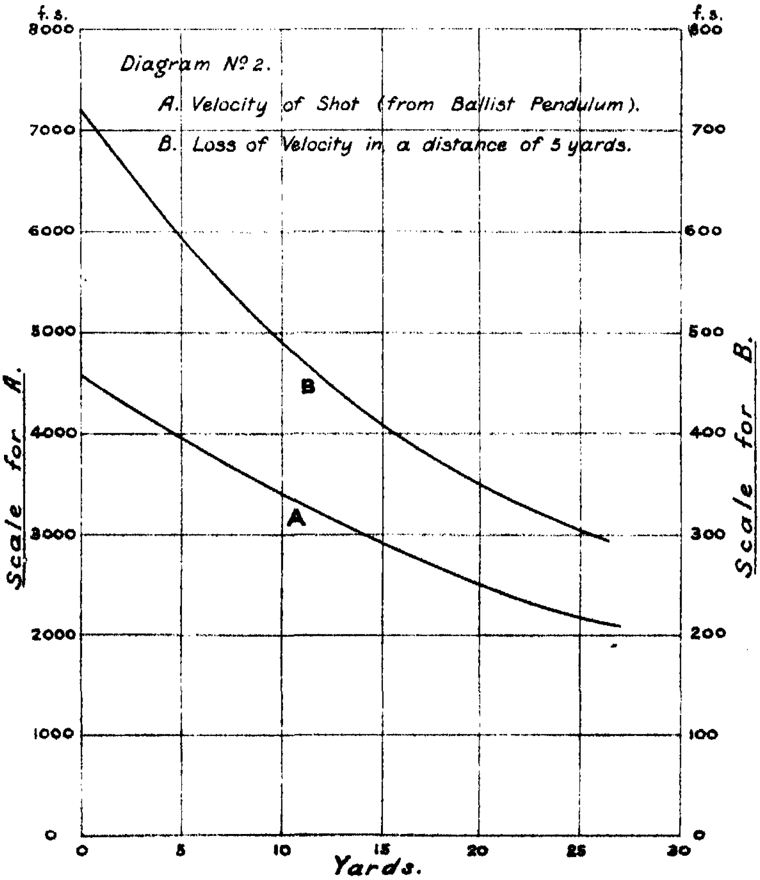
* I hope to determine the true value more accurately than I have hitherto had time to do. Probably it is not a constant for all velocities, but approximates to a constant as the velocity increases.

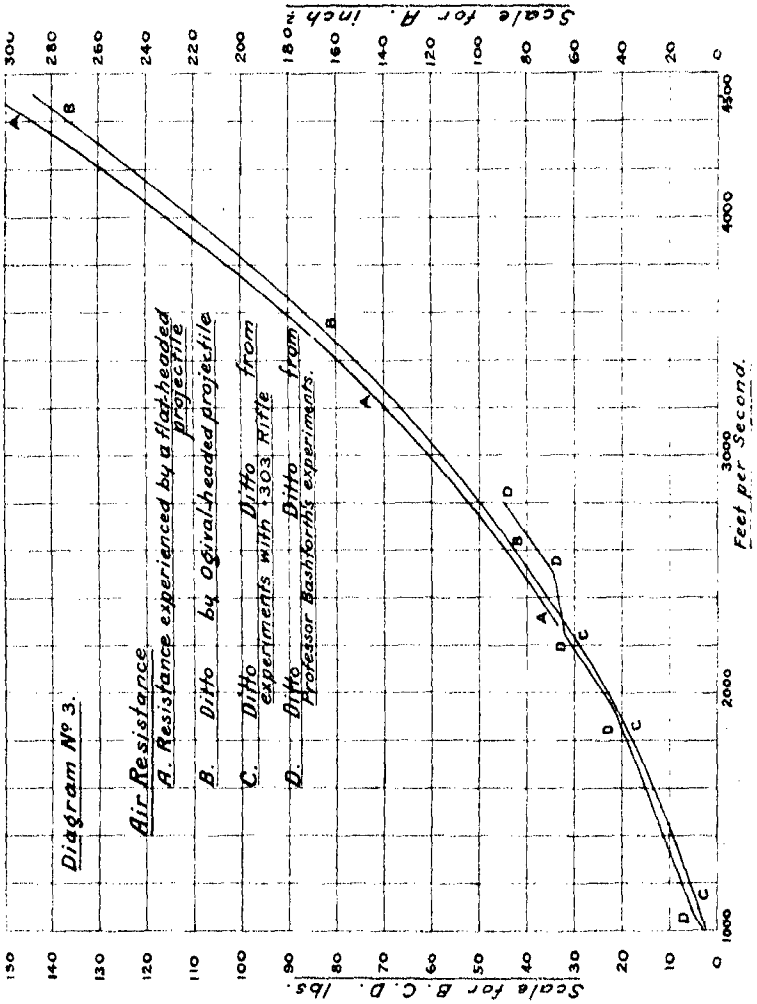
When it is considered that the latter were obtained with projectiles weighing many pounds, and the others with shot of 23 and 215 grains respectively, the close agreement of the resistance curves is very satisfactory, and shows in a striking way what can be done with small scale experiments when the proper scale of dynamic similarity is employed.

FIG. 2.



The extended resistance curve presents no peculiarities, although it can only be expressed at present by an arbitrary formula. But that this should be so is in itself rather remarkable, for it might well have been expected that the resistance would, for high velocities at least, be proportional to the pressure requisite to cause a gas to discharge through a hole in a thin-walled vessel at the speed of the shot.

FIG. 3.



The pressure in question is $\left(1+\frac{\gamma-1}{2}\frac{v^2}{a^2}\right)^{\frac{\gamma}{\gamma-1}}$, where a is the velocity of sound, but the curve represented by this function and the curve of actual resistance do not even tend to approximate:

"Theory of Amphoteric Electrolytes. Part II." By JAMES WALKER, F.R.S., University College, Dundee. Received October 19,—Read November 17, 1904.

In a previous paper* it was shown that if HXOH is an amphoteric electrolyte, it is possible to express the concentration of the various ions present in aqueous solution in terms of the concentration of the unionised substance, the dissociation constants of the substance acting as acid and as base respectively, and the ionisation constant of water. As the expressions obtained will be frequently used in the present paper, I reproduce them here in their original form, suitable for calculation when the electrolyte is preponderantly acid, and also in the form which would be used when the substance is preponderantly basic. The active masses of the various substances present at equilibrium are represented as below, the dissociation constants of acid, base and water being denoted by k_a, k_b, and K respectively—

$$\begin{array}{ccccc} \mathrm{H}^+ & \mathrm{OH}^- & \mathrm{XOH}^- & \mathrm{HX}^+ & \underbrace{\mathrm{HXOH}+\mathrm{X}} \\ a & b & c & d & u \end{array}$$

$$a = \sqrt{\frac{\mathrm{K}+k_a u}{1+k_b u/\mathrm{K}}} \;\ldots\ldots\ldots\ldots (1). \qquad a = \mathrm{K}/b \;\ldots\ldots\ldots\ldots (1').$$

$$b = \mathrm{K}/a \;\ldots\ldots\ldots\ldots (2). \qquad b = \sqrt{\frac{\mathrm{K}+k_b u}{1+k_a u/\mathrm{K}}} \;\ldots\ldots\ldots\ldots (2').$$

$$c = k_a u/a \;\ldots\ldots\ldots\ldots (3). \qquad c = \frac{k_a}{\mathrm{K}}ub \;\ldots\ldots\ldots\ldots (3').$$

$$d = \frac{k_b}{\mathrm{K}}ua \;\ldots\ldots\ldots\ldots (4). \qquad d = k_b u/b \;\ldots\ldots\ldots\ldots (4').$$

It was further shown that in the case of the amino-benzoic acids investigated by Ostwald and by Winkelblech an application of the theory accounted for the abnormalities exhibited by these acids, and in particular led to the deduction of values of the molecular conductivity which were in satisfactory accordance with those observed. A thorough recalculation of the results shows that the more strictly the theory is applied the better is the correspondence between theory and experiment. Owing to a systematic error in the first calculation, the values given for d were, when the ratio k_b/K was large, somewhat too high, the total concentration $\eta = 1/v$ having been taken in the calculation by inadvertence equal to $u+a+d$ instead of equal to $u+a+2d$. The latter result is deduced as follows:—The total concentration, corresponding to the composition of the solution as made up in the ordinary way, is evidently the sum of the concentrations of the substances containing X, since this by hypothesis undergoes neither association nor dissociation. The total concentration is therefore

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* 'Roy. Soc. Proc.,' vol. 73, p. 155, 1904; also 'Zeitschrift für physikalische Chemie,' vol. 49, p. 82.

$$\eta = u + c + d, \quad \text{or} \quad \eta = u + a + 2d,$$

since $b + c = a + d$,* and b is vanishingly small in an acid solution.

The following table contains the values of a and d multiplied by 10^5, and is an extended and corrected form of the table given on p. 160 of the original paper, for which it is to be substituted.

$k_a = 10^{-5}$.

v.	$k_b/K = 0$.		$k_b/K = 1$.		$k_b/K = 10$.		$k_b/K = 100$.		$k_b/K = 1000$.	
	a.	d.	a.	d.	a.	d.	a.	d.	a.	d.
1	316	0	224	223	95·3	934	31·5	2960	9·99	8330
10	100	0	95	8·5	70·5	69·0	30·1	283	9·94	880
100	31·2	0	31·0	0·3	29·7	2·9	22·0	20·6	9·44	79
1,000	9·5	0	9·5	0·0	9·4	0·1	9·06	0·8	6·73	5·5
10,000	2·71	0	2·71	0·0	2·70	0·01	2·69	0·02	2·61	0·18

This table shows even more plainly than the original one the peculiarities noted in the previous paper. When the numbers it contains are used to calculate the apparent dissociation constant k_0, it is found that the values up to $k_b/K = 10$ undergo no alteration (p. 162). The new values for the other ratios are as follows:—

$k_0 \times 10^5$ calculated from $\alpha = a + d/5$ and $\alpha = a + d/6$.

v.	$k_b/K = 100$.		$k_b/K = 1000$.	
	$a + d/5$.	$a + d/6$.	$a + d/5$.	$a + d/6$.
10	0·756	0·602	3·15	2·22
100	0·700	0·662	0·65	0·52
1000	0·936	0·930	0·67	0·63

These numbers are only slightly different from those previously obtained.

Turning now to the calculation of k_0 for the amino-benzoic acids, the following improved method of ascertaining the value of the constant k_a, which is here not readily accessible to direct experiment, may be noted. Previously this value was adjusted to correspond with the experimental value of k_0 obtained at $v = 1024$, the greatest dilution investigated, for in the cases under consideration the constants k_0 and k_a approximated most closely at this degree of dilution. This advantage, however, is more than counterbalanced by the drawback that here the experimental errors due to conductivity of the water, oxidation at the electrodes, etc., are at a maximum. In the recalculation, therefore, the adjustment of the k_a value was made from a consideration of the most concentrated instead of the most dilute solutions in order that the effect of these experimental errors might, as far as possible, be eliminated. This readjustment has in every case improved the concordance between the experimental and theoretical values of the conductivity, as a comparison of the subjoined tables with those previously given (pp. 164–5) will show.

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* *Loc. cit.*, p. 158.

o-Amino-benzoic Acid.

$k_b/\mathrm{K} = 112$, $k_a = 1{\cdot}04 \times 10^{-5}$, $\mu_\infty \mathrm{H^+, XOH^-} = 357$,
$\mu_\infty \mathrm{HX^+, XOH^-} = 70$.

v.	*a*.	*d*.	μ, calc.	μ, expt.	$k_0 \times 10^5$, calc.	$k_0 \times 10^5$, Ost.	$k_0 \times 10^5$, Wink.
64	24·0 × 10^{-5}	89·1 × 10^{-5}	7·24	7·21	0·66	0·66	0·65
128	20·4	16·6	10·8	10·8	0·74	0·74	0·74
256	16·3	6·6	16·2	16·2	0·84	0·84	0·84
512	12·4	2·5	23·6	28·6	0·92	0·91	0·92
1024	9·1	0·89	33·8	33·7	0·97	0·97	0·96

p-Amino-benzoic Acid.

$k_b/\mathrm{K} = 210$, $k_a = 1{\cdot}21 \times 10^{-5}$, $\mu_\infty \mathrm{H^+, XOH^-} = 356$,
$\mu_\infty \mathrm{HX^+, XOH^-} = 68$.

v.	*a*.	*d*.	μ, calc.	μ, Ost.	μ, Wink.	$k_0 \times 10^5$, calc.	$k_0 \times 10^5$, Ost.	$k_0 \times 10^5$, Wink.
32	22·3 × 10^{-5}	132·7 × 10^{-5}	5·42	—	5·48	0·74	—	0·74
64	20·9	62·1	7·46	7·58	7·49	0·71	0·72	0·71
128	18·7	27·8	10·95	10·86	11·12	0·76	0·75	0·79
256	15·8	11·7	16·42	16·34	16·84	0·88	0·87	0·91
512	13·5	4·55	24·37	24·24	26·29	0·98	0·98	1·06
1024	9·4	1·68	35·40	35·01	36·86	1·07	1·05	1·17

m-Amino-benzoic Acid.

$$k_b/\mathrm{K} = 1100,\quad k_a = 1{\cdot}63 \times 10^{-5},\quad \mu_\infty \mathrm{H}^+,\mathrm{XOH}^- = 355,$$
$$\mu_\infty \mathrm{HX}^+,\mathrm{XOH}^- = 66.$$

v.	a.	d.	μ, calc.	μ, Wink.	$k_0 \times 10^5$, calc.	$k_0 \times 10^5$, Wink.
64	$11{\cdot}75 \times 10^{-5}$	$159{\cdot}0 \times 10^{-5}$	9·38	9·36	1·12	1·12
128	11·37	77·0	11·68	11·72	0·87	0·88
256	10·70	36·2	15·84	16·04	0·81	0·84
512	9·64	16·2	23·00	23·40	0·88	0·91
1024	8·20	6·81	34·40	35·24	1·02	1·07

Even in the case of the meta-acid, where the experimental error due to oxidation is greatest, the agreement is remarkably close.

Where the ionised proportion is great, *i.e.*, where u is no longer approximately equal to η, the evaluation of the concentrations of the various components in the solution is troublesome. In order that for any case likely to occur, an idea of the magnitude of u may be obtained, I append a table which gives values of $u/\eta = uv$, *i.e.*, of the unionised proportion of the electrolyte, under a considerable number of different conditions.

$$uv = u/\eta \text{ for } k_a = 10^{-4}.$$

v.	$k_b/\mathrm{K} = 1$.	$k_b/\mathrm{K} = 10$.	$k_b/\mathrm{K} = 100$.	$k_b/\mathrm{K} = 1000$.	$k_b/\mathrm{K} = 10{,}000$.
0·1	0 980	0·940	0·833	0·613	0·333
1	0·980	0·940	0·833	0·613	0·333
10	0·965	0·937	0·833	0·613	0·333
100	0·904	0·893	0·822	0·612	0·333
1,000	0·730	0·727	0·707	0·584	0·331
10,000	0·382	0·382	0·380	0·364	0·277

It will be noted that the preceding table only gives uv for the acid constant $k_a = 10^{-4}$. From the table it is not, however, difficult to find uv for other values of k_a. If, for example, it is desired to find v for a given value of u, we may make use of the following relation, r being used to denote the ratio k_b/K:—

$$\eta = u + a + 2d, \qquad \eta - u = a\,(1 + 2ru).$$

Now, if we consider another amphoteric electrolyte with another k_a, but the same k_b, we have

$$\eta' - u = a'\,(1 + 2ru),$$

but since r and u are identical in both equations, we obtain by division

$$\eta' - u = \frac{a'}{a}(\eta - u).$$

If we are dealing with an electrolyte of markedly acid character, we may, in the expression for a, neglect K in comparison with $k_a u$,* and so obtain

$$a = \sqrt{\frac{k_a u}{1 + ru}}, \qquad a' = \sqrt{\frac{k'_a u}{1 + ru}}, \qquad \frac{a'}{a} = \sqrt{\frac{k'_a}{k_a}}.$$

Finally, therefore, we have

$$\eta' = u + \sqrt{\frac{k'_a}{k_a}}(\eta - u).$$

Given then the values of η and u for one k_a, we may easily calculate the value of η (or of r) for another k_a if u and r remain unaltered.

One is generally confronted, however, with the converse problem of determining u for a given value of v, but the table may again be utilised in virtue of the following considerations. Neglecting K in comparison with $k_a u$, we may write as before

$$\eta - u = a + 2aru,$$

or, multiplying both sides by v and re-arranging,

$$uv = \frac{1 - av}{1 + 2ra}.$$

Substituting the value of a in terms of u and the constants, we obtain

$$uv = \frac{1 - v\sqrt{\dfrac{k_a u}{1 + ru}}}{1 + 2r\sqrt{\dfrac{k_a u}{1 + ru}}},$$

or

$$uv = \frac{1 - v\sqrt{\dfrac{k_a uv}{v + ruv}}}{1 + 2r\sqrt{\dfrac{k_a uv}{v + ruv}}}.$$

If we now denote the product uv by p, re-arrange, square, and express in powers of p, we obtain as result

$$(r - 4k_a r^2)p^3 + (v - 2r - 4k_a rv)p^2 + (r - 2v - k_a v^2)p + v = 0.$$

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* Compare *loc. cit.*, p. 156.

Finally, if we denote the reciprocal of k_a by l, and divide throughout by v, we have

$$\left(\frac{r}{v}-\frac{4r^2}{lv}\right)p^3+\left(1-\frac{2r}{v}-\frac{4r}{l}\right)p^2+\left(\frac{r}{v}-2-\frac{v}{l}\right)p+1 = 0.$$

The coefficients of p are here homogeneous functions of v, r, and l of degree zero, that is, we do not by altering v, r, and l in the same ratio effect any change in the value of p. In other words, if we increase the constant k_a n-fold, and simultaneously diminish v and r (or k_b) in the same proportion, the unionised proportion remains unaltered.

The following is an example of the employment of the preceding table in conjunction with this result. Suppose it is desired to know the value of $u'v'$ for $k'_a = 10^{-3}$, $k'_b/\mathrm{K} = 100$, $v' = 10$. The table gives the values for $k_a = 10^{-4}$. We must therefore, in consulting the table, increase k'_b/K and v' in the same ratio as that in which k'_a is diminished, that is, we must find the value in the table for $k_b/\mathrm{K} = 1000$ and $v = 100$. The number sought is $uv = u'v' = 0{\cdot}612$, whence $u' = 0{\cdot}0612$.

The conclusion that the unionised proportion is unaffected by a simultaneous change of $1/k_a$, k_b, and v in the same ratio is of importance in the discussion of the ionisation of a series of amphoteric electrolytes in which the product k_ak_b is constant. Ostwald* ascertained that the influence of a substituent on the dissociation constants of simple acids is of such a character that the constant of each acid is increased or diminished for a given substitution in a ratio, which, although not constant for different acids, is usually of the same order in a series of similar substances. The same rule no doubt holds good for bases, although in this case accurate data are wanting. At all events we know that when chlorine is substituted for hydrogen in a simple acid, the dissociation constant of the acid is greatly increased, and we also know that when the same substitution is made in a simple base, the strength of the base is greatly diminished. Suppose now that the substitution takes place in an amphoteric electrolyte. We might expect the primary effect to be a considerable increase in the value of k_a and a corresponding diminution in the value of k_b. This primary effect would, however, in many cases be complicated by stereo-chemical influences, and possibly by the secondary influence which the change in the strength of the acid group might exert on the strength of the basic group, and conversely. Winkelblech found in opposition to this, that the substitution of methyl for hydrogen in glycine diminished the acidic and basic constants simultaneously, and the same is true of the effect of isomerism in the amino-benzoic acids. In these examples it may be that the primary effect is masked by the superimposed secondary effects, for in the analogous case of the continued methylation of the amino-benzoic acids, the acid parent substances are finally converted into derivatives of pronouncedly basic character. The detailed investigation of these methyl derivatives is at present proceeding in my laboratory.

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* 'Zeitschrift für physikal. Chem.,' vol. 3, p. 171 (1889).

Turning now to the theoretical discussion of the simple case in which the product $k_a k_b$ remains constant in a series of amphoteric acids, we find that the dilution at which a given ionisation occurs, becomes greater as the constants approximate, or, in other words, that at a given dilution the unionised proportion uv increases as k_b approaches k_a in value. From the table on p. 274 it will be seen that the influence of dilution on the proportion unionised is comparatively small at ordinary dilutions when the value of k_b is considerable. From this it follows that in the region considered a ten-fold increase in k_a with a corresponding diminution of k_b may have no appreciable effect on the product uv at the *same* v, although from equation (4) the proportion of H^+ compared with HX^+ will be greatly increased. Here then we have with a nearly constant unionised proportion, considerable variation in the relative proportions of the ions present, not only in the case of a given acid at different dilutions, but also at the same dilution in a series of acids with varying constants, if the product of the acid and basic constants remains invariable. This comparative constancy of uv often greatly simplifies its evaluation in a given case. Suppose that in the series of amphoteric substances with constant $k_a k_b$ we consider that one for which $k_a = k_b$. This substance will be absolutely neutral, and its ionisation, and therefore its uv, will be the same at all dilutions (compare previous paper, p. 159). Here the calculation of uv is easy, since $c + d = 2d$ gives the ionised quantity, and $a = b = \sqrt{K}$. Equation (4) then becomes $d = ku/\sqrt{K}$, and since $v^{-1} = u + 2d$,

$$uv = \frac{\sqrt{K}}{\sqrt{K} + 2k}.$$

Now at 25° $K = 1{\cdot}2 \times 10^{-14}$, so that for this temperature

$$uv = \frac{1{\cdot}095 \times 10^{-7}}{1{\cdot}095 \times 10^{-7} + 2k} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5).$$

To exemplify this mode of calculation we may take the case considered on p. 276. We wish to know the value of uv, for $k_a = 10^{-3}$, $k_b/K = 100$, and $v = 10$. Here $k_b = 1{\cdot}2 \times 10^{-12}$ and $k_a k_b = 1{\cdot}2 \times 10^{-15}$. A substance with the same product $k_a k_b$ but with $k_a = k_b$ would have $k = \sqrt{1{\cdot}2 \times 10^{-15}} = 0{\cdot}3465 \times 10^{-7}$. Applying formula (5) we obtain $uv = 0{\cdot}613$, a very close approximation to the true value 0·612.

The method of calculation here indicated becomes inapplicable only at great dilutions and in cases where the two constants are very widely apart. In any case it affords a useful first approximation to the value of u, and gives the limit to which uv may attain in maximo at increasing concentrations.

If, in the table on p. 274 we interchange k_a and k_b, the values of uv remain unaltered. We are now, therefore, in a position to consider the whole series of amphoteric electrolytes with a constant product k_ak_b, beginning with a practically simple acid (*i.e.*, with a substance whose k_b is of small dimensions compared with K) and ending with a practically simple base (*i.e.*, with a substance whose k_a is small compared with K). As k_a diminishes and k_b increases, the total ionisation falls off rapidly at first, thereafter more slowly until through a comparatively large range it is practically constant at the minimum value which is actually reached when $k_a = k_b$. At this point we are dealing with an absolutely neutral substance. As k_a still further diminishes and k_b correspondingly increases, the ionisation begins to increase slowly at first, and the substances considered become more and more basic in character. Finally the ionisation increases rapidly, and we deal at last with what is practically a simple base.

In applying the preceding results it is essential to bear in mind that they have been obtained on the assumption that K may be neglected in comparison with k_au in dealing with an amphoteric acid, and with k_bv in dealing with an amphoteric base. Should, therefore, the preponderant constant or the total concentration be very small, due allowance must be made for this neglect.

Since the publication of my previous paper, Mr. John Johnston, B.Sc., has made in my laboratory some experiments on the conductivity of asparagine and of cacodylic acid, two well-marked amphoteric electrolytes of character somewhat different from the amino-benzoic acids already investigated.

Asparagine is of special interest, inasmuch as both its acidic and basic constants have been determined by Winkelblech from hydrolysis experiments on the two types of salts to which it gives rise. The values found by him were $k_a = 5{\cdot}2 \times 10^{-9}$ and $k_b/\text{K} = 150$. Calculating from these values and adopting $\mu_\infty \text{H}^+, \text{XOH}^- = 355$ and $\mu_\infty \text{HX}^+, \text{XOH}^- = 66$, in accordance with the method previously described, we obtain as the molecular conductivity at $v = 16$ the number 0·087. The value obtained directly by Walden* was 0·541 Winkelblech† also determined the molecular conductivity, and found numbers some 40 per cent. smaller than those of Walden, although he still considers them too great. The reason of the discrepancy is the very small value of the conductivity of asparagine, any conducting impurity either in the substance itself or in the solvent water having a very great relative effect. At my request Mr. Johnston carefully purified a specimen of asparagine by repeated recrystallisation from water until the conductivity showed no further diminution on repetition of the process. He ascertained that with a specimen which might be accounted pure in the ordinary analytical sense no less than twenty-four recrystallisations were required to reduce the conductivity to a constant value unaffected by further recrystallisation. The solvent water employed during the last crystallisations and in the determination of the conductivity was purified in the manner described by Walker and Cormack.* The constant molecular conductivity of asparagine found with this water at $v = 16$ was 0·096. This experimental number is still somewhat too great owing to the impossibility of removing all conducting impurity from the water, the error due to this cause being probably of the dimensions of one-tenth of the total conductivity.† In view of the experimental error, then, the agreement between the values calculated and found is as close as could be expected.

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* 'Zeitschrift für physikal. Chem.,' vol. 8, p. 483, 1891.

† *Loc. cit.*, vol. 36, p. 568, 1901.

The results in the case of cacodylic acid have been published by Mr. Johnston elsewhere,‡ and are also in satisfactory accordance with the theory, which has thus been tested by conductivity and hydrolytic experiments in a range of k_a from 5×10^{-9} to $1 \cdot 6 \times 10^{-5}$, and of k_b/K from 32 to 1100.

An interesting theoretical point arises in connection with cacodylic acid, the formula of which is generally written $(CH_3)_2\,AsO.OH$. This formula does not come under the general formula H.X.OH, which is applicable to the amino-acids, inasmuch as the only replaceable hydrogen atom it contains is that of the hydroxyl group. The distinction between these two classes of amphoteric electrolytes has already been pointed out by Ostwald.§ From the standpoint of the theory just put forward, however, it is unnecessary to consider it, for as long as the unionised substance is not subject to molecular association, the theory is applicable without modification to either class. The freezing-point determinations of Zawidzki show that this condition is fulfilled for cacodylic acid.

With regard to the freezing-point depression and correlated phenomena exhibited by non-associating amphoteric electrolytes, the following points may be noted. Since the production of HX^+ and XOH^- from H.X.OH in the first class, or of Y^+ and YO^- from Y.OH in the second class, involves no change in the total number of molecules, this type of dissociation is not connected with any alteration in the freezing point of the solution. The production of H^+ and OH^- on the other hand increases the total number of molecules, and in consequence the freezing-point depression. We may say briefly, then, that the acidic or basic ionisation of an amphoteric electrolyte increases the freezing-point depression or any derived magnitude, whereas the "saline" ionisation does not. Taken in conjunction with the electric conductivity, the cryoscopic method should yield results of utility with soluble electrolytes whose ionisation is considerable. As a means of determining the extent to which acidic or basic ionisation, as distinguished from saline ionisation, has taken place, measurements of electromotive force with hydrogen electrodes may, in some instances, be applied with success. Experiments in this direction are at present in progress.

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* 'Journ. Chem. Soc.,' vol. 77, p. 8, 1900.

† Compare Walker and Cormack, *loc. cit.*, p. 18.

‡ 'Berichte Deut. chem. Ges.,' vol. 37, p. 3625, 1904.

§ 'Zeitschrift für Elektrochemie,' vol. 6, p. 36, 1899.

"The Electrical Conductivity and other Properties of Sodium Hydroxide in Aqueous Solution, as elucidating the Mechanism of Conduction." By WILLIAM ROBERT BOUSFIELD, M.A., K.C., M.P., and THOMAS MARTIN LOWRY, D.Sc., Lecturer in Physical Chemistry and Crystallography at the Central Technical College. Communicated by Professor H. E. ARMSTRONG, F.R.S. Received June 24,—Read November 17, 1904.

(Abstract.)

The original object of the research was to investigate the decay, as the temperature rises, in the "ionising" properties of water; which is manifest, especially in the case of the alkalies, in the inflected character of the curves expressing the relation between temperature and conductivity in aqueous solutions.* It was found, however, that the available data for the physical properties generally of the alkalies were very few; the inquiry was, therefore, extended so as to include the measurement of the density and conductivity of solutions of sodium hydroxide at 18° C., as well as of the temperature co-efficients of conductivity and density. The great viscosity of the more concentrated solutions being very noticeable, measurements of viscosity were also made, in order to correlate this property with the low conductivity of these solutions. The principal results of the investigation are as follows:—

(1) In the most dilute solutions, in which "ionisation" is nearly complete, the curves expressing the relation between molecular conductivity and temperature are not inflected between 5° and 100° C. They resemble the curves representing the changes in viscosity with temperature in dilute aqueous solutions. Concentrated solutions also give curves that are not inflected. In these solutions a very rapid increase of conductivity takes place as the temperature is raised: the conductivity of a 50-per-cent. solution

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* Compare 'Roy. Soc. Proc.,' 1902, vol. 71, pp. 42—54.

increasing 5-fold between 0° and 18° and 80-fold between 0° and 100° C.; the form of the conductivity-temperature curves again appears to be determined mainly by molecular changes rendered apparent in the rapid changes of viscosity which accompany changes of temperature. Moderately dilute solutions give curves that are inflected between 0° and 100°; a regular curve can be drawn connecting the temperature of inflection with the percentage of sodium hydroxide in the solution: this temperature reaches a minimum, at 48° C., in the case of a normal (4 per cent.), solution, but rises to 100° C. when the concentration is raised to 30 per cent.

(2) The inflected conductivity-temperature curves can be represented by the simple cubic formula

$$\kappa_t = \kappa_0 + \alpha t + \gamma (t - \tau)^3,$$

where τ is the temperature of inflection. As this formula is unsatisfactory when applied to curves that are not inflected between 0° and 100° C., a formula was devised which was based upon the three factors of concentration, ionisation and ionic mobility, on which the variations of specific conductivity depend. The influence of temperature on the density, and therefore on the concentration, has been experimentally determined and can be directly allowed for; in order to express the influence of temperature on the other two factors, it has been assumed that the variation of ionic mobility with temperature may be expressed by a formula similar to that of Slotte for the variation of fluidity

$$\eta_0/\eta = (1 + bt)^n,$$

and that the decay of ionisation with rising temperature may be expressed by a formula similar to that of Abegg and Seitz for the decrease in the dielectric constant

$$D/D_0 = e^{-at}.$$

The formula $\frac{\kappa_t}{\kappa_0} = \frac{\rho_v}{\rho_0} (1 + bt)^n e^{-at}$, which has been used to express the influence of temperature on conductivity, has the advantages that it is applicable to conductivity-temperature curves of all kinds, that a definite physical meaning can be given to each of the constants, and that it gives expression, not only to the inflection now under consideration, but also to the maximum conductivity and the second inflection in the general conductivity-temperature curve.* What is, perhaps, of even greater importance, is the fact that it has been found possible, with the help of this formula, to make some approximation to resolving the two opposing influences which determine the form of this curve.

(3) The density tables for caustic soda, in general use until about 10 years ago, were based on the early measurements of Dalton and of

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* *Loc. cit.*, p. 52.

Tünnermann (1827). A revised table was published by Hager in 1883, but the first table in which even the second place of decimals is correctly given is that of Pickering (1894). Pickering's solutions were prepared from purified material, but were standardised by titration, and can therefore be relied on only to the third place of decimals. The re-determination of the densities was undertaken in order to obtain a method of standardisation that should be more accurate than titration. Quantities of sodium, amounting to about 150 grammes at a time, were weighed, and converted quantitatively into concentrated solutions of sodium hydroxide by the action of steam in a platinum vessel. Eleven determinations, made with six different standard solutions, gave, as the density of a 50-per-cent. solution, the value 1·5268, with an average error of 0·0001. Solutions of known concentrations having been prepared by dilution, their densities were determined; it was then possible, by measuring the density, to determine the percentage of sodium hydroxide in any pure solution, with an error only one-tenth as great as that introduced in standardising by titration. This method contributed greatly to the accuracy of the electrical measurements; in the absence of such a method, the measurements of some of the earlier investigators have been vitiated by errors in the concentration, amounting to as much as 2 per cent. on the total weight of alkali in the solution.

(4) The determination of the conductivity at 18° C. of solutions prepared in this way led to results which, although slightly different from the earlier observations of Kohlrausch, gave a curve of similar form. The maximum conductivity at 18° C. is 0·3490 in a 15-per-cent. solution, the value given by Kohlrausch being 0·3462. At higher temperatures the maximum conductivity is considerably greater, rising to over 1·4 at 100°, and occurs in solutions of greater concentration.

(5) The viscosity of a 50-per-cent. solution of sodium hydroxide is approximately seventy times as great as that of water. This increase of viscosity must produce a large effect on the ionic mobility; the influence of this factor may be to some extent eliminated by dividing the molecular conductivity by the fluidity, and this ratio we have called the "intrinsic conductivity" of the solution. Whilst the molecular conductivity of sodium hydroxide solutions decreases steadily as the concentration is increased, the intrinsic conductivity falls to a minimum at about 8 per cent. NaOH, and then rises, until at 50 per cent. NaOH, the value is considerably greater than in the most dilute solutions. It is believed that this increase is due to the fact that liquid soda is an electrolyte, *per se*, and that, in concentrated solutions, the current is conveyed partly by the soda alone, as if it were in the fused state.

(6) A study of the influence of temperature on the density revealed the fact that the addition of soda produces a simplification in behaviour

that may be attributed to the destruction by the soda of the ice-molecules present in the water. In the formula

$$\rho_t = \rho_0 + \alpha t + \beta t^2 + \gamma t^3,$$

which represents the influence of temperature on the density of water and aqueous solutions of soda, the coefficient of t^3 vanishes when a concentration of 12 per cent. NaOH is reached, whilst the coefficient of t^2 vanishes at 42 per cent. NaOH; at the latter concentration there is a simple linear relationship between density and temperature.

(7) The molecular volume of sodium hydroxide in dilute aqueous solution has a large negative value, a litre of water dissolving 140 grammes of sodium hydroxide at 0°, 100 grammes at 18°, or 60 grammes at 50°, without increasing in volume. It is noteworthy that the molecular volume does not increase continuously as the temperature rises, but reaches a maximum value at about 70° C. In a 50-per-cent. solution, however, the temperature has little effect on the molecular volume, the extreme variation being only about 10 per cent.

"The Refractive Indices of the Elements." By CLIVE CUTHBERTSON.

Communicated by Professor F. T. TROUTON, F.R.S. Received October 18,—Read November 24, 1904.

(Abstract.)

In a letter addressed to 'Nature,' in October, 1902, attention was drawn to the fact that the refractivities of the five inert gases of the atmosphere, He, Ne, A, Kr, and X, as determined by Ramsay and Travers, were, within narrow limits of accuracy, in the proportion of 1, 2, 8, 12 and 20; or, more simply, of $\frac{1}{4}$, $\frac{1}{2}$, 2, 3, and 5.

In a second letter it was shown that the refractivities of the halogens, Cl, Br, and I, stand also in the relation of 2, 3, and 5 to the same degree of accuracy; but it was pointed out that the figures for P, As, and S, as measured by M. Le Roux in 1861, did not show any similar relation; and it was observed that a redetermination of them would be interesting.

With a Jamin's refractometer, adapted for use with high temperatures, results have now been obtained for Hg, P, and S, which differ widely from those of M. Le Roux. The index of mercury, calculated for a molecule containing two atoms, is placed at 1·001857, a number which agrees closely with the value given by the refractive equivalent of Gladstone. The index of P_2 is found to be 1·001197 and that of S_2 is 1·001101.

In all three cases it is estimated that the margin of error does not

exceed 1½ per cent. Comparing these values for P_2 and S_2 with those of N_2 and O_2, it is shown that the simple relations found in the case of the inert gases and the halogens also hold in the case of nitrogen and phosphorus, oxygen and sulphur; and that an atom of phosphorus retards light four times as much as an atom of nitrogen, an atom of sulphur four times as much as an atom of oxygen.

Efforts have also been made to measure the index of fluorine in the gaseous state, but, owing to the experimental difficulties, success has not yet been attained.

It appears then, that, out of fourteen elements whose index of refraction has been measured in the gaseous state, twelve conform to the rule that in each chemical group the refractivities of the elements are in the ratios of small integers. The other two, Hg and H, have no allied elements with which they can be compared.

It is pointed out that N, O, and Ne are each followed, in their respective families, by an element whose refractivity is four times as great, and that, consequently, there are reasons for believing that the elements composing the series N, O, F, and Ne, and P, S, Cl, and A are, in some sense, homologous. Comparing the refractivities of the latter series we see that the power to retard light appears to be closely connected with the valency, increasing as it increases, in spite of the decrease in atomic weight, as shown in the following table:—

	Element.			
	P.	S.	Cl.	A.
Atomic weight	31	32	35·5	40
Refractivity	299 × 4	275 × 4	192 × 4	141 × 4

The series Ne, O, N, show the same relation, and it is probable that the refractivity of C is even higher than that of N.

The refractivity of B, estimated from BCl_3 and BBr_3, is certainly very great; but whether it exceeds that of C there is not sufficient evidence to determine.

"Some Physical Characters of the Sodium Borates, with a New and Rapid Method for the Determination of Melting Points."

By CHARLES HUTCHENS BURGESS and ALFRED HOLT, Junr.

Communicated by Professor H. B. DIXON, F.R.S. Received October 27.—Read November 24, 1904.

Some time ago we published a note* containing some new observations on the solubility of metallic oxides in fused boric anhydride. Since its publication we have been further studying some of the points therein mentioned, but have been in part anticipated by W. Guertler,† who has examined many of the phenomena we remarked, in a more complete manner. As, however, our experiments do not cover exactly the same ground as his, we have arranged in the following paper the results relating to the sodium borates, which we believe are completely new, and, at the same time, present many interesting features towards the study of these complex bodies.

When a quantity of ordinary pure borax glass is heated for some hours at a temperature which gives it about the consistency of a thick syrup, it gradually changes to a mass of colourless crystals. The crystallisation begins at two or three points on the surface of the mass, generally around a particle of dirt, or minute fragment of imperfectly fused borax, and spreads in more or less spherulitic growths throughout the glassy portion. As the crystals grow, there appears to be a contraction of volume, since the glass around them appears as raised hummocks, and a subsequent investigation of the specific gravities of the crystals and glass showed that this was really the case.

The crystals do not seem to grow at a uniform rate. They start rapidly, but as development continues, they take longer and longer to form, so that many hours are occupied in changing from pure glass to a holocrystalline aggregate.

We have not been able to isolate any individual crystals, and so study their characters, but the whole crystalline mass appears to be composed of dense, matted clusters of very minute needles, which are doubly refracting, and have a pearly lustre. They are about as soluble in water as ordinary borax glass, are not hygroscopic, and melt at a higher temperature than the glass, into which they are reconverted on melting, and then cooling quickly.

We find, however, that it is not borax glass alone which exhibits this phenomenon of crystallisation on reheating, but that the glasses obtained by fusing mixtures of boric anhydride and sodium carbonate, in which the ratio of the boric anhydride to the sodium carbonate is not 2 : 1, also exhibit it in varying degree.

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* 'Journ. Chem. Soc. Proc.,' 1903, p. 221.

† 'Zeit. Anorg. Chem.,' vol. 40, 2, pp. 225 and 268; vol. 40, 3, p. 337.

Thus, all mixtures in which the ratio varies from 6 : 1 to 8 : 5, give a glass when fused, and are all capable of being changed completely into crystals on reheating, exactly like borax. Mixtures in which the boric anhydride is present in greater proportion than 6 : 1, only change with difficulty on prolonged heating; and when they do, the crystals are always found to be mixed with more or less truly glassy material, till, when the ratio 40 : 1 is reached, it seems impossible to obtain crystals at all. So far as we can ascertain, a mixture of this composition is always a true glass in any circumstances.

Mixtures, on the other hand, in which the ratio of boric anhydride is less than 8 : 5, when fused, and allowed to cool, yield nearly opaque, white substances, which seem to be micro-crystalline. Nevertheless, these mixtures if heated to a high temperature, and then suddenly chilled by being poured into mercury, also yield glasses.

The glasses obtained by this sudden chilling seem to be very unstable, as on gently heating by means of a Bunsen flame, they change completely, and almost instantaneously, into crystals.

There seems then to be a gradual alteration in the rapidity and completeness with which this change occurs, and as it seemed probable that the crystallisation of some borate rich in sodium was the cause of it, we proceeded to determine what was the composition of the borate richest in sodium which could be obtained by fusing boric anhydride with sodium carbonate.

When boric anhydride is fused with sodium carbonate, carbon dioxide is evolved, and the product may be regarded as boric anhydride combined with sodium oxide (Na_2O). Thus, by heating boric anhydride with a large excess of sodium carbonate, and determining the amount of carbonate decomposed, the greatest proportion in which boric anhydride combines with sodium oxide can be ascertained, and ought to give the composition of the richest sodium borate obtainable by fusion.

We have performed this experiment several times, and have obtained the following results :—

(i) One part of B_2O_3 combines with 1·29 parts Na_2O
(ii) One „ „ 1·34 „
(iii) One „ „ 1·32 „

These results are probably a little too low, as the sodium carbonate loses some carbon dioxide merely on heating alone, but this amount is negligible, and does not in any way affect the conclusion that the product obtained in this way is not sodium metaborate ($NaBO_2$), in which the ratio of boric anhydride to sodium oxide is 1 : 1, and that sodium orthoborate (Na_3BO_3), in which the ratio is 1 : 3, cannot in any case be formed by fusion of boric anhydride and sodium carbonate.

The object of the research became thus threefold:—

(*a*) To determine what compounds are present in crystals obtained with various mixtures of boric anhydride and sodium carbonate;

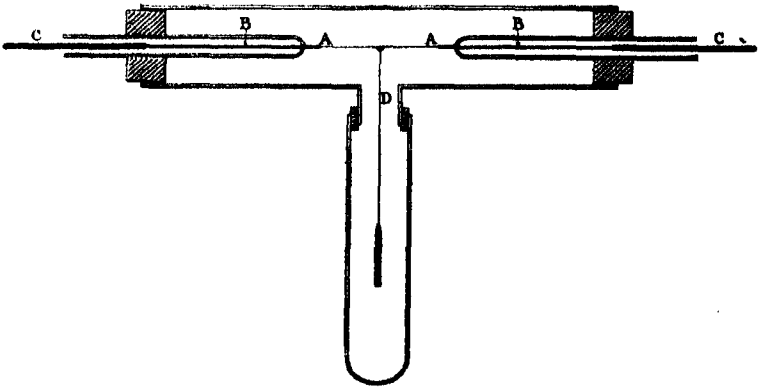
(*b*) What is the nature of the glass;

(*c*) What is the nature of the change from glass to crystals.

The most obvious method seemed to be to determine the melting points of crystals and glasses of varying composition, to see if compounds existed, and to compare and correlate the melting point curves obtained. To do this it was necessary to employ some new melting point method, as none is known by which the melting point of glasses can be determined at all accurately.

We devised an apparatus which is somewhat similar to the "meldometer" described by Joly,* and we found it to be both rapid and peculiarly suitable in the case of plastic substances, which have hitherto been supposed to possess no definite melting point.† Our apparatus is represented in fig. 1.

FIG. 1.



A uniform piece of platinum wire, AA, about 4 cms. long, was welded to two stouter pieces of the same metal, BB. These were sealed into two thin glass tubes, and were welded to two thick copper wires, CC, which conveyed the current. The whole was fixed by two rubber stoppers in a glass tube, with an opening at D.

A small bead of the material whose melting point was desired, was made on one end of a very thin platinum wire, to which a weight of about a gramme was attached.

A current of 4—6 ampères was passed through the wire AA so as to raise its temperature considerably above that at which the bead melted. The bead was then inserted through the opening D, when on touching the wire it became fused. The current was switched off, and the bead, on solidifying, remained attached to the edge of the wire AA. Air currents were prevented by closing the opening D with a test-tube.

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* 'Roy. Irish Acad.,' 1889.

† We use the words "melting point" to denote the sudden decrease in viscosity which occurs at a very well defined temperature in glasses.

A slowly increasing current was then passed through the wire till the portion of the bead in contact with it melted, when the weight and bead fell into the test-tube. The moment this occurred, the voltage between the ends of the wire and the ampères passing through it were carefully noted. From the values obtained the resistance was calculated, and thence the temperature.

The weight hanging from the bead had no decided effect on the melting point. We found that with weights varrying from 0·2—5 grammes, the bead dropped off at practically identical temperatures. This temperature at which beads of various compounds drop off the wire is extremely well defined, even in the case of substances which become plastic on heating, like glass, so that provided no chemical change occurs during the heating, the method proved rapid and elegant. A certain amount of heat is conducted away by the ends of the thick platinum wires BB to which the thinner one AA is welded, and also by the bead itself. It, therefore, became necessary to calibrate the wire by means of pure salts of known melting points.

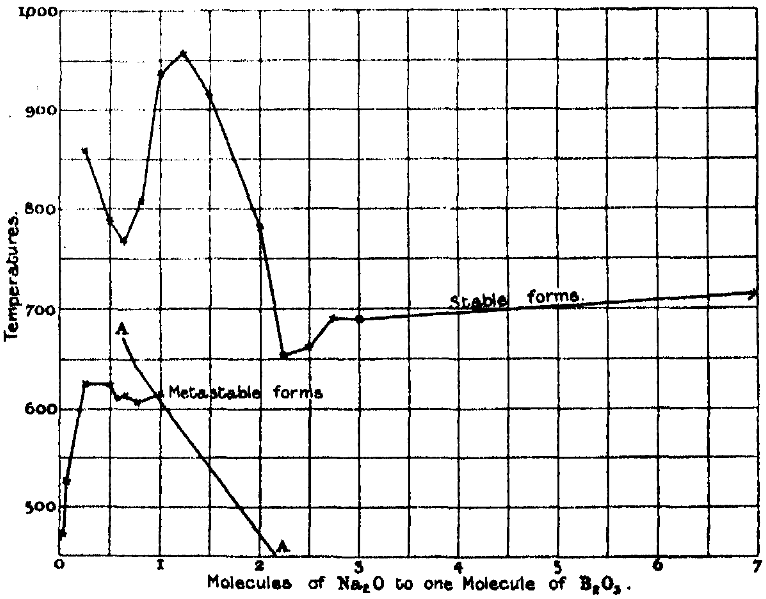
We found this was a matter of some difficulty, as very many of the most ordinary salts were found to decompose to some extent on heating. Sodium chloride, sodium carbonate, potassium iodide, calcium chloride, and strontium chloride all underwent change. Of these salts sodium chloride was very little attacked, but after only a few minutes' fusion we found it had absorbed quite an appreciable amount of oxygen, being converted into the peroxide. Potassium iodide changed in part to iodate, sodium carbonate to the peroxide, and calcium and strontium chlorides to the oxides.

These changes completely prevented any accurate melting point determinations, so after repeated trials we adopted potassium nitrate, lithium chloride, and potassium chloride as standards. It is true that potassium nitrate decomposes on heating, but as the nitrite (to which it changes) has almost the same melting point, the small amount of change was found to be immaterial. The chlorides we employed seemed to be, on the whole, very stable.

The melting points given in Carnelley's tables for these three standard substances were assumed as correct; they were used in fixing three points on the temperature-resistance curve.

Thus, any temperature between the melting points of potassium nitrate and potassium chloride could be obtained by interpolation from the measured resistance, and those above the melting point of potassium chloride by extrapolation. The results did not seem to contain an error larger than 1 per cent., so that we considered the method was satisfactory enough. The melting point curves for the glasses and crystals are represented on fig. 2. The curve for the glasses presents some features which are difficult to explain, since, so far as we are aware, no such curve has before been described.

FIG. 2.



The addition of sodium oxide to boric anhydride raises the melting point continuously till a mixture of composition $Na_2O.4B_2O_3$ is reached. There seems to be no depression of the melting point at all, thereby differing from the case of ordinary solution, and indicating the probability that there is no solid phase.

The curve then remains fairly level till a composition $Na_2O.2B_2O_3$ is reached, when it falls irregularly to $3Na_2O.4B_2O_3$.

The last point we could obtain on this curve was with composition $Na_2O.B_2O_3$, where the melting point practically coincided with the temperature of change from the glassy to the crystalline state of this mixture. Indeed it is a little above it, but it was possible by fairly rapid heating to melt the bead before the change had occurred.

At present we are unable to state exactly what the meaning of this melting point curve for the glasses may be. Glasses have hitherto been supposed to possess no sharp melting point, but this does not seem to be the case, as our results for each different temperature were remarkably close and well defined.

The melting point curve for the crystals is more easily explainable than that of the glass.

We were unable to obtain any point on it between pure boric anhydride and a mixture of composition $Na_2O.4B_2O_3$. This was because the crystallisation of the small mass of substance in the beads we employed for the melting point determinations took an extremely long time, and also because the devitrification was never complete except in the neighbourhood of the mixture $Na_2O.4B_2O_3$.

From a mixture of composition $Na_2O.4B_2O_3$ the melting point falls nearly uniformly till $5Na_2O.8B_2O_3$ is reached, at which point it begins to rise rapidly. The mixture $5Na_2O.8B_2O_3$ would then appear to be a marked eutectic point.

The summit of the curve is reached with composition $5Na_2O.4B_2O_3$, when it falls again to a mixture which may be considered to have the composition $5Na_2O.4B_2O_3 + 4Na_2CO_3$, and which represents the eutectic point between $5Na_2O.4B_2O_3$ and Na_2CO_3.

The further addition of sodium carbonate causes a gentle, almost uniform rise in the melting points.

As the summit occurs with composition $5Na_2O.4B_2O_3$, and as this very nearly agrees with the analysis of the borate richest in sodium, which can be obtained on fusion of boric anhydride and sodium carbonate, this would seem to indicate a compound.

The results of these melting point determinations of the crystalline mixtures indicate that borax ($Na_2O.2B_2O_3$) is not a definite compound in this state, but is almost a eutectic mixture of the borate with composition $5Na_2O.4B_2O_3$ and one of composition $Na_2O.4B_2O_3$, for the existence of which we have other evidence.

This melting point curve for the crystalline forms of these various mixtures cannot be regarded as truly representing either the *solidus* or *liquidus*. It seems probable that in this case they are situated close to each other, and that our melting points really represent temperatures close to the liquidus. The fact that a mass of crystals would apparently melt almost completely at an almost constant temperature certainly indicates that there cannot be any very great difference between the liquidus and solidus, and, as in the cases studied by Heycock and Neville, that the actually determined melting points lie probably very near to the liquidus.

The following table gives the melting points for the various glasses and crystals :—

	Melting point.	
Composition of mixture.	Glass.	Crystals.
B_2O_3	468°	—
$Na_2O.40B_2O_3$	470	—
$Na_2O.16B_2O_3$	528	—
$Na_2O.4B_2O_3$	628	858°
$Na_2O.2B_2O_3$	628	791
$9Na_2O.16B_2O_3$	613	—
$5Na_2O.8B_2O_3$	620	777
$3Na_2O.4B_2O_3$	610	815
$Na_2O.B_2O_3$	615	930
$5Na_2O.4B_2O_3$	—	960
$5Na_2O.4B_2O_3 + Na_2CO_3$		917
$5Na_2O.4B_2O_3 + 3Na_2CO_3$	—	783
$5Na_2O.4B_2O_3 + 4Na_2CO_3$	—	654
$5Na_2O.4B_2O_3 + 5Na_2CO_3$	—	664
$5Na_2O.4B_2O_3 + 6Na_2CO_3$	—	692
$5Na_2O.4B_2O_3 + 7Na_2CO_3$	—	685
$5Na_2O.4B_2O_3 + 27Na_2CO_3$	—	722

We have analysed a number of the glasses and crystals obtained with various mixtures, and obtained most unexpected and interesting results.

The analysis of a borate is always a matter of difficulty, but we found the following method worked quite well, and gave accurate results. A weighed quantity of the substance (glass or crystals in very fine powder) was evaporated to dryness twice with fairly strong hydrochloric acid. By this means all the sodium was converted into the chloride. The dry powder thus obtained was repeatedly treated with small quantities of methyl alcohol, and evaporated to dryness. By this means all traces of hydrochloric acid were removed, as well as the whole of the boracic acid, so that pure sodium chloride remained. This was dissolved in water and estimated by titration with N/10 silver nitrate solution, using potassium chromate as indicator.

The complete separation of the crystals from the glass was by no means an easy matter. We found that quite the easiest and most satisfactory method was to crush up the substance into coarse powder, and then to pick out with forceps the really glassy fragments and the crystalline masses. This was quite easy by using a lens.

Though the crystals and glass have different specific gravities, it was not found possible to obtain a real separation by means of a heavy liquid. This was because pieces of material which looked wholly crystalline often contained glass in the interior, so that they would float anywhere in the liquid.

We also tried extraction with hot methyl alcohol which is a solvent for boric anhydride, for, if the crystals had been due to a separation of a borate from its solution in boric anhydride, this should have left the compound pure. As a matter of fact we found that the methyl alcohol decomposed both the crystals and glass, giving methyl borate, boracic acid, and sodium methylate. Both glass and crystals were decomposed at the same rate.

Attempts to use water as a means of separation were also failures, since the solubility of both glass and crystals is about the same.

The results of our analyses are as follows :—

(i) *Mixture of Composition about* $Na_2O.2B_2O_3$.—This mixture crystallised completely in a few hours, giving a hard, white, completely crystalline mass. When about two-thirds had crystallised the glass and crystals were separated, and gave on analysis :—

Glass = 30·9 per cent. Na_2O ; crystals = 31·0 per cent. Na_2O.

(ii) *Mixture of Composition about* $3Na_2O.8B_2O_3$.—This crystallised completely, and had the same characters as (i).

On analysis obtained :—

Glass = 25·86 per cent. Na_2O ; crystals = 25·81 per cent. Na_2O.

(iii) *Mixture of Composition about* $Na_2O.4B_2O_3$.—This crystallised completely, and had the same characters as (i).

On analysis obtained :—

Glass = 18·70 per cent. Na_2O ; crystals = 18·67 per cent. Na_2O.

(iv) *Mixture of Composition about* $Na_2O.6B_2O_3$.—This crystallised very nearly completely, but seemed to contain small translucent glass-like fragments.

On analysis obtained :—

Glass = 11·5 per cent. Na_2O ; crystals = 13·7 per cent. Na_2O.

(v) *Mixture of Composition about* $Na_2O.8B_2O_3$.—This did not crystallise completely. After very prolonged heating it nearly all changed to a crystalline mass with an almost waxy lustre, but which was not really wholly crystalline. There was always in addition a portion of the mass which remained a glass.

On analysis obtained :—

Glass = 10·06 per cent. Na_2O ; crystals = 11·90 per cent. Na_2O.

(vi) *Mixture of Composition about* $Na_2O.12B_2O_3$.—Only about half would crystallise, and this took a very long time.

On analysis obtained :—

Glass = 2·1 per cent. Na_2O ; crystals = 12·2 per cent. Na_2O.

(vii) *Mixture of Composition about* $Na_2O.16B_2O_3$.—After heating this mixture for several days only a very small amount crystallised.

On analysis obtained :—

Glass = 4·18 per cent. Na_2O; crystals = 10·02 per cent. Na_2O.

(viii) *Mixture of Composition about* $Na_2O.40B_2O_3$.—This could not be crystallised at all.

From these numbers it appears that with mixtures between $Na_2O.4B_2O_3$ and $Na_2O.2B_2O_3$ the crystals and glass have absolutely identical composition, but with mixtures containing more boric anhydride than $Na_2O.4B_2O_3$, only a part (decreasing in quantity as the amount of boric anhydride present increases) crystallises, and this part has approximately the composition $Na_2O.6B_2O_3$.

As the crystals of the mixture of this composition contain more sodium than the glass, it seems probable that, could one obtain the crystals really pure and not entangling any glass, the composition might approach that of $Na_2O.4B_2O_3$.

The nearness in composition of the crystals obtained from mixtures varying from $Na_2O.16B_2O_3$ to $Na_2O.6B_2O_3$ makes it seem fairly certain that it is the same compound which separates out in all of them, and that the differences in the analyses are due to the crystals being mixed with more or less glass which it was impossible to remove. In experiment (vi) the crystals and glass were particularly well separated, and the result is shown by the great difference in their analyses.

It seemed so curious that with mixtures of composition $Na_2O.2B_2O_3$ to $Na_2O.4B_2O_3$ the glass and crystals should give similar analytical results, that we thought it worth while to try fractional crystallisation of the glasses, to see if we could detect any differences between the different crystalline portions.

The analyses of these various portions gave the following results :—

(i) *For a mixture of composition about* $Na_2O.2B_2O_3$—

		Per cent. Na_2O.
First portion	glass	= 29·7
	crystals	= 29·3
Second portion	glass	= 29·9
	crystals	= 29·2
Third portion	glass	= 30·3
	crystals	= 30·5
Fourth portion	glass	= 30·2
	crystals	= 30·1

(ii) *For a mixture of composition about* $Na_2O.4B_2O_3$—

		Per cent. Na_2O.
First portion	glass	= 18·7
	crystals	= 18·6
Second portion	glass	= 18·6
	crystals	= 18·4

We also fractionally crystallised borax itself five times, when the final crystalline portion was found to contain 30·8 per cent. Na_2O, theory for $Na_2B_4O_7$ requiring 30·7 per cent. Na_2O.

These differences are negligible, and the crystals that separate out *from the glass have exactly the same composition from the beginning.*

These results show at once that this crystallisation is not due to the separation of any single compound as we had previously supposed, but that it is more probably due to the formation of mixed crystals or a solid solution from a superfused liquid.

All the various crystalline fractions obtained from any one glass of composition $Na_2O.4B_2O_3$ to $Na_2O.2B_2O_3$ were found to melt at identical temperatures, as also did the residual glasses. Further, the crystalline portions when melted, gave glasses which had a melting point identical with that of the previous residual glass, and these residual glasses could, in their turn, be changed to crystals with similar melting points to those which had originally been separated.

This shows most conclusively the identity of the crystals and glass in chemical composition. We have also determined in the case of several mixtures the temperatures at which this crystallisation takes place. The curve indicating these temperatures is shown in fig. 2 by the line joining AA.

A bead of the glass was put on the platinum wire of our melting point apparatus, and the temperature raised extremely slowly, whilst the bead was watched with a lens. In the case of those mixtures which melted before the change occurred, no weight was attached to the bead. The crystallisation appeared to start at a fairly well defined temperature, and, if it was maintained, would gradually spread through the bead.

It is a little hard to say exactly what is the meaning of this curve AA, fig. 2, and all that seems certain is that it gives approximately the temperatures at which the rate of crystallisation assumes a sufficient velocity to visibly change the state of the substance.

From a consideration of the melting point curves, together with the analytical and other observations we have described, it is possible to form some idea as to the nature of these glasses and the crystals into which they are wholly or partially transformable.

The glass must be regarded as a superfused, and, therefore, metastable form of the crystals, behaving in several respects as if it were a liquid of enormous viscosity.

Now, on considering the behaviour of the glasses ranging in composition from pure boric anhydride to $Na_2O.6B_2O_3$, it will be noticed that the supposition of the existence of a borate of about the composition $Na_2O.5B_2O_3$, which is dissolved in boric anhydride, will explain the observed facts. A mixture of composition $Na_2O.40B_2O_3$ cannot be crystallised at all, and one of composition $Na_2O.16B_2O_3$ only partially crystallises, hence some point between these mixtures will give the maximum solubility of this borate in boric anhydride. On further increasing the amount of this borate present, the glass becomes a supersaturated and superfused liquid, the amount of crystallisation measuring the supersaturation.

Somewhere between $Na_2O.6B_2O_3$ and $Na_2O.4B_2O_3$ no free boric anhydride remains in the solution, and the whole mass will crystallise for the first time.

On further addition of sodium, another borate of composition near $5Na_2O.4B_2O_3$ begins to be formed, and we have shown that in any mixture between these two compounds, both crystals and glass have identical compositions. We are here probably dealing with a case of solid solution, and the glass is merely its superfused form.

The character of the curve would indicate that there are two types of crystals, one rich in B_2O_3, the other rich in Na_2O, and the lowest point of the curve is the eutectic point formed by mixtures of these two.

That the crest of the curve does not occur with the composition $Na_2O.B_2O_3$ can be most conveniently explained by the fact that solid solutions cannot be treated as pure substances, and so a slight shifting of the maximum point is to be expected. The further depression of the melting point curve probably indicates the eutectic point between these crystals, rich in Na_2O, and sodium carbonate.

In conclusion we wish to express our thanks to Professor H. B. Dixon and Mr. D. L. Chapman, for the kindly interest they have taken in our work.

"On the Group IV Lines of Silicium." By Sir NORMAN LOCKYER, K.C.B., LL.D., Sc.D., F.R.S., and F. E. BAXANDALL, A.R.C.Sc.

Received October 11,—Read November 17, 1904.

[PLATES 11 AND 12.]

In previous communications to the Royal Society* an account was given of the behaviour of the lines of silicium under varying experimental conditions, and as a result of this enquiry, the lines were divided into four distinctive groups.

In these papers no reproductions of the silicium spectra were given, a description of the behaviour of the lines in the various photographs being at the time considered sufficient.

The genuineness of the lines of Group IV, as silicium lines, has recently been questioned by M. de Gramont. In his paper† he gives an account of the effect of self-induction on the various groups of lines into which the silicium spectrum was divided from a study of the Kensington photographs. He also gives an analysis of these lines with regard to their appearance in stellar spectra. He agrees as to Groups I, II, and III, but states that the lines of Group IV always disappear from his spectra with the air lines, and he concludes from this that they are not genuine lines of silicium, but belong to either oxygen or nitrogen. This conflicts so much with the conclusions arrived at from the investigations of the Kensington photographs that it becomes necessary to give the photographic evidence on which the lines were accepted as being due to silicium.

The wave-lengths of the lines of Group IV are 4089·1, 4096·9, and 4116·4. Of these three, 4096·9 is quite insignificant in intensity compared with the other two, and as it is so weak as not to be shown in the reproductions of the photographs, it may well be left out of the present discussion. It may here be stated that, according to Neovius, there is a weak and diffuse oxygen line (Intensity 1) at λ 4089·2, and a weak nitrogen line (Intensity < 1) at λ 4116·7; which are very nearly the positions of the silicium lines. Whether these are the lines which M. de Gramont gets in his spectra—he records both in his lists as very faint—it is not possible to say, but that they are not the lines which appear in the Kensington photographs will probably be readily admitted when the reproductions of the spectra in the present paper are carefully examined.

The spectrum A shown in Plate 11 is that given by an electric discharge in a vacuum tube containing silicium tetra-fluoride. The bottom portion is that from the incandescent gases in the bulb of the

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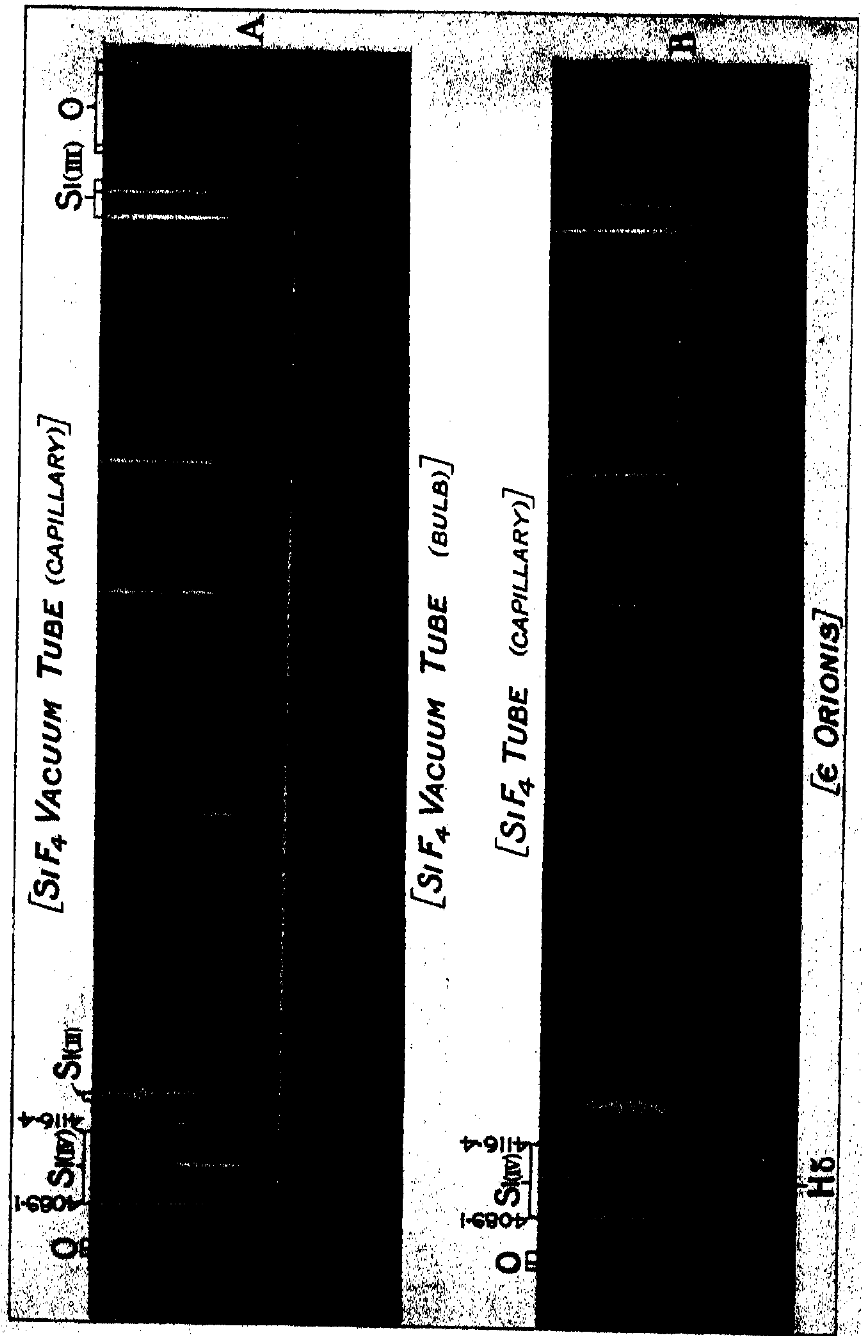
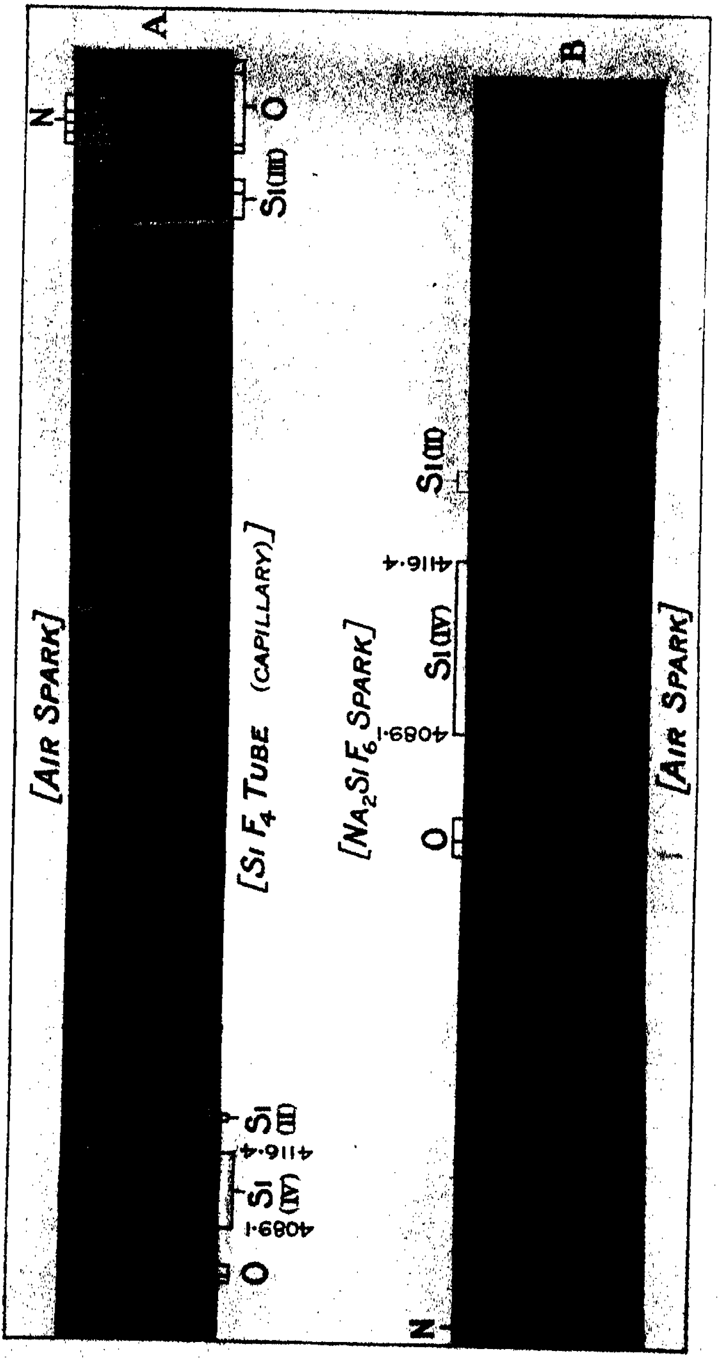
* 'Roy. Soc. Proc.,' vol. 65, p. 449; vol. 67, p. 403.

† 'Comptes Rendus,' vol. 139, p. 188.


A
Si(III)
O
[SiF$_4$ Vacuum Tube (Capillary)]
Si(III)
4116·4
Si(IV)
4089·1
O
B
[SiF$_4$ Vacuum Tube (Bulb)]
[SiF$_4$ Tube (Capillary)]
4116·4
Si(IV)
4089·1
O
[ε Orionis]
Hδ


A
N
O
Si (III)
[Air Spark]
[Si F4 Tube (Capillary)]
O
4089·1
Si (IV)
4116·4
Si (III)
B
Si (III)
4116·4
Si (IV)
4089·1
O
[Na2 Si F6 Spark]
[Air Spark]
N

tube, the top that from the capillary, both photographed during the same exposure. The transverse white line represents the junction of the spectra of the bulb and capillary. In the top portion the silicium lines of Groups II, III, and IV, are well seen, and also the ordinary lines of oxygen, these being indicated in the reproduction. The triplet marked O is one of the most conspicuous features of the spark spectrum of oxygen, and the individual lines are, according to Neovius, the strongest in the oxygen spectrum. It will be seen that the Si IV line 4089·1 is stronger than any of the oxygen triplet lines, while the line 4116·1 is about as strong as the latter. As the oxygen and nitrogen lines of Neovius which occur near these lines are of intensity (1) and (<1) respectively, it is evident that if the lines ascribed to Si IV in the Kensington spectra are really due to air, as M. de Gramont contends, they must undergo a remarkable transformation as regards intensity in passing from the conditions of the ordinary spark spectrum to those of the vacuum tube. There is, however, no indication of the selective enhancement of these faint air lines in the Kensington spectra of air under the vacuum tube conditions.

It will be instructive to trace the behaviour of these different sets of lines in the two portions of the spectrum shown in Plate 11. It will be noticed that in the bottom or bulb portion of the spectrum the oxygen triplet survives, though it is very weak. The Si IV lines, however, one of which is stronger in the top spectrum than the oxygen lines, have entirely disappeared. As to the silicium lines of Groups II and III, they are represented in the bulb spectrum; both sets, however, being weaker than in the capillary spectrum, the weakening in intensity being more marked in the case of Group III than Group II. It is thus seen that the conditions appertaining to the gases in the bulb are conducive to the existence of the lines of Group II; less so to those of Group III; and not at all to those of Group IV.

In B of Plate 11 the SiF_4 spectrum is reproduced alongside that of ε Orionis. The identity of position of the oxygen triplet and Si IV lines with lines in the stellar spectrum is there denoted. It may here be stated that the stellar and terrestrial spectra do not exactly fit throughout their whole length, owing to the fact that they were obtained with different prisms.

In A of Plate 12 the spectrum shown in the top part of A Plate 11 is compared with the ordinary spark spectrum of air. The lines 4089·1 and 4116·4 of Si IV, which are strongly marked in the vacuum tube spectrum, are entirely lacking in the air spectrum, although the oxygen triplet previously referred to is common to both spectra and of about equal intensity in each.

In B of Plate 12 the spark spectrum of sodium silico-fluoride, volatilised between platinum poles, is compared with the spectrum of air, also made incandescent between platinum poles. In each spectrum the ordinary lines of oxygen and nitrogen are well seen. The silicium lines 4089·1 and 4116·4, denoted in the reproduction, are shown in the top spectrum, but they are entirely lacking in the air spectrum at the bottom. It would be remarkable that these lines, if really due to air, should not appear in the air spectrum itself. Moreover, the lines do not appear in the spark spectra of any of the chemical elements investigated other than silicium, although in all these the ordinary air lines are always well shown.

To sum up, the lines of Group IV have never been noted in any Kensington spectra without being accompanied by silicium lines of other groups, and they never appear unless silicium in some form or other is used in the light source furnishing the spectrum.

With regard to their identity with stellar lines, whatever their true terrestrial origin may be, there is scarcely any doubt. They agree exactly in wave-length with very strong lines in the spectra of the belt stars of Orion, and with less conspicuous lines in many other stellar spectra, for which no other satisfactory origin has been suggested.

"On Chemical Combination and Toxic Action as exemplified in Hæmolytic Sera."*

By Robert Muir, M.D., Professor of Pathology, University of Glasgow, and Carl H. Browning, M.B., Ch.B., Carnegie Research Fellow, University of Glasgow.

Communicated by Dr. C. J. Martin, F.R.S. Received November 10,—Read December 1, 1904.

It is now well known that the action of a hæmolytic serum depends upon two substances, viz.: (*a*) the immune-body, which is developed as the result of the injection of the red corpuscles of an animal of different species, and (*b*) the complement, a labile substance which is present in the serum of the normal animal, and which is not increased as the result of such injection. Ehrlich has pointed out the similarity in the constitution of complements and of various toxins, and our own observations strongly support his views. We may, in the study of hæmolysis, consider the complement as a toxin, the red corpuscles treated with the appropriate immune-body as the object on which the toxin is to act, and the hæmolysis as the indication of the toxic action. Ehrlich regards the complement as consisting of two chief atom-groups, the haptophore or combining group and the zymotoxic; but in speaking of the action of sera he does not always carry out this distinction completely. For example, the efficiency of different complements as tested by their hæmolytic or bacteriolytic effects is often taken as

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* The expenses of this research were defrayed by a grant from the Carnegie Trustees.

evidence of the degree of chemical affinity between the complements and the immune-body. But it is manifest that theoretically a complement may combine perfectly through the medium of the immune-body, and yet produce little hæmolysis, owing to the absence of sensitiveness to the zymotoxic group—combination or "complementing" may occur and yet hæmolysis be deficient or absent. The question which we have investigated is accordingly this—Where different complements differ in their action as shown by the dosage, both of complement and of immune-body required, does this depend upon differences in their combining affinities or upon differences in their toxicity?

In working out this problem we have made use of three sera, viz.: (*a*) the serum of the rabbit injected with ox's corpuscles, therefore hæmolytic towards ox's corpuscles, (*b*) the serum of the rabbit injected with guinea-pig's corpuscles, (*c*) the serum of the guinea-pig injected with rabbit's corpuscles. In each case the hæmolytic serum is deprived of its complement by heating at 55° C. and, therefore, contains only immune-body; it is accordingly inactive until complement (*i.e.*, normal serum) is added.

In this and the other tables the following abbreviations are used: IB = immune body, and *v.* is placed before the name of the animal on whose corpuscles the immune-body acts, thus *IB rabbit v. guinea-pig* signifies the immune-body obtained from the rabbit, and acting on guinea-pig's corpuscles, C = complement, 1D = one hæmolytic dose (of IB or C as the case may be).

In the first place, we may give in tabular form, the average dosage of the several complements with the different immune sera: the test amount of corpuscles being 1 c.c. of a 5-per-cent. suspension in 0·8 per cent. sodium chloride solution.

Immune-body and corpuscles tested.	Rabbit's complement.	Guinea-pig's complement.	Ox's complement.
IB rabbit *v.* ox Ox's corpuscles	0·15 c.c.	0·025 c.c.	∞
IB rabbit *v.* guinea-pig Guinea-pig's corpuscles	0·15 „	0·8 „	0·03 c.c.*
IB guinea-pig *v.* rabbit Rabbit's corpuscles	0·5 „	0·07 „	0·04 „ *

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* The normal serum of the ox has a strong hæmolytic action both on rabbit's and on guinea-pig's corpuscles. This is due to the presence of a natural immune-body, and it is not possible to remove this in the usual way by placing the serum in contact with the corpuscles at 0° C. We have, however, made allowance for this circumstance, and the dosage of complement has been calculated accordingly, and may be taken as substantially correct.

This table shows that in the cases studied the highest dosage of the complement of an animal occurs when used against its own corpuscles.

Dosage of Immune-bodies with different Complements.

Complement.	IB rabbit *v.* ox.	IB rabbit *v.* guinea-pig.	IB guinea-pig *v.* rabbit.
Rabbit's	0·003 c.c.	0·003 c.c.	0·15 c.c.
Guinea-pig's	0·003 "	0·03 "	0·015 "
Ox's	∞	?[*]	0·02 "

The most striking facts brought out in this table concern the relative doses of immune-bodies with rabbit's and guinea-pig's complements respectively, they are (*a*) in the case of an immune-body acting on the corpuscles of another animal (viz., ox's corpuscles), its dose with rabbit's complement is practically the same as that with guinea-pig's complement; (*b*) when the immune-body acts on guinea-pig's corpuscles its dose is ten times greater with guinea-pig's complement than with rabbit's complement, and a converse statement obtains in the case of the immune-body to rabbit's corpuscles. It is also to be noted that the immune-body to ox's corpuscles does not bring about complete hæmolysis at all when the ox's complement is used.

These tables supply the hæmolytic doses of the different immune-bodies and complements; they do not, however, give us the facts with regard to their several combinations. In illustration of this we may mention that Ehrlich and Morgenroth,[†] finding that the dose of the immune-body to rabbit's corpuscles obtained from the guinea-pig was ten times higher (as shown in the table) when rabbit's complement was used than when guinea-pig's complement was used, supposed that there were really two immune-bodies, one present in large amount taking up guinea-pig's complement and another present in small quantity taking up rabbit's complement. This is manifestly a satisfactory theoretical explanation, but we have to enquire whether it is supported by facts.

We shall accordingly consider the amounts of complement taken up through the medium of different doses of immune-body in the several cases. It will be convenient to take first the second and third sera, as above arranged. The method employed for estimating the amount of complement taken up depends upon the firmness of union of complement, and has been described in former papers.*

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[*] We have not succeeded in getting a satisfactory estimation of the dose of this immune-body with ox's complement, owing to failure to remove the natural immune-body for guinea-pig's corpuscles in the ox's serum.

[†] Ehrlich and Morgenroth, 'Berlin. klin. Woch.,' 1900, No. 31.

I. *Immune-body to Guinea-pig's Corpuscles (obtained by injecting the Rabbit with these corpuscles).*

(a) *With Guinea-pig's Complement—*

We may first compare the results when guinea-pig's complement is used, with those when rabbit's complement is used. In the former case the dose of complement is very high; in fact, more than ten times the amount of guinea-pig's complement sufficient to hæmolyse ox's corpuscles, is necessary to hæmolyse its own corpuscles. This might be due to the fact that only a fraction of the complement molecules suited the immune-body to guinea-pig's corpuscles, or it might be due merely to weakness of toxic action of the complement. If the former were the case the presence of the uncombined complement would be shown by adding the corpuscles of another animal treated with the corresponding immune-body. The matter is put to the test by adding varying amounts of guinea-pig's complement to guinea-pig's corpuscles with their corresponding immune-body, and then after allowing 2 hours at 37° C. for combination, to test for the presence of complement by means of ox's corpuscles treated with their immune-body. If we use 1 D of immune-body to indicate the amount necessary to produce lysis when rabbit's complement is used, then 10 D will be the M.H.D. when guinea-pig's complement is used. The following are the chief results which we have obtained. It is to be noted that, of course, if less than 10 D is added complete lysis does not occur with guinea-pig's complement, and in such cases the tubes are centrifugalised and the clear fluid is added to the indicator, *i.e.*, ox's corpuscles treated with their immune-body. This indicator is specially suitable on account of the high sensitiveness of the corpuscles to guinea-pig's complement.

Such an experiment may be graphically represented thus—

$$\text{Guinea-pig's } \bigcirc + n\,\text{IB} + x \text{ guinea-pig's C } \vdots \; + \text{Ox's } \bigcirc + \text{IB}$$

the small circle indicating red corpuscles, the vertical dotted line a period of incubation at 37° C., n indicating a definite multiple of IB, and x varying amounts of C.

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* Muir, 'The Lancet,' 1903, vol. 2, p. 446; and Muir and Browning, 'Roy. Soc. Proc.,' June 9, 1904.

IB Rabbit *v.* Guinea-pig. Guinea-pig's C.

Experiment XLII.—2 D of IB took up 0·08 c.c. guinea-pig's C.
8 " " 0·288 " "
Dose of guinea-pig's C = about 0·3 c.c.

" XLIII.—1 D of IB took up 0·026 c.c. guinea-pig's C.
5 " " 0·114 " "
10 " " 0·254 " "
Dose of C = 0·25 c.c.

" XLIV.—1 D of IB took up 0·014 c.c. guinea-pig's C.
14 " " 0·38 " "
Dose of C = 0·35 c.c.

" LXIX.—1 D of IB took up 0·04 c.c. guinea-pig's C.
5 " " 0·28 " "
10 " " 0·48 " "
Dose of C = 0·4 c.c.

From these results it is manifest that the large amount of guinea-pig's complement necessary to produce lysis, combines completely with the guinea-pig's corpuscles treated with the corresponding immune-body, there being, up to a certain point, no complement left over to act on the test corpuscles, and the large dose of immune-body necessary is simply due to this amount being required to bring the necessary complement into combination with the corpuscles. The guinea-pig's complement has, therefore, a *weak toxic action* on guinea-pig's corpuscles, about ten times weaker than it has, for example, on ox's corpuscles.

Note.—The amount of complement taken up is calculated from the point at which free complement is obtainable after time has been allowed for combination. It will be noticed that the amount of complement taken up is approximately, though not strictly, proportional to the amount of immune-body present. The divergence is more marked when higher multiples are used, as has been noted by one of us in the case of another combination; in other words, what is known as "Ehrlich's phenomenon," is seen to a slight extent. As, however, there is very little evidence of dissociation of complement after it has combined, the phenomenon in this case is probably due to presence of complementoid.

(b) *With Rabbit's Complement*—

It will be seen from the tables that (*a*) the M.H.D. of immune-body in this case is small—about a tenth of that necessary when guinea-pig's complement is used, and (*b*) that the dose of complement also is comparatively small, in fact, practically the same as that necessary for the hæmolysis of ox's corpuscles. In investigating the amount of rabbit's complement taken up by means of multiple doses of immune-body, interesting and at first very puzzling results emerged. An experiment of this kind may be graphically represented as before, thus :—

Guinea-pig's ○ + n IB + x rabbit's C : Guinea-pig's ○ + IB.

In performing experiments of this kind we found that five or even ten doses of immune-body apparently led to the taking up of scarcely more complement than one dose of immune-body did; and further that the amount of complement apparently taken up seemed to become less, the longer the test corpuscles were left in the fluid. Thus, for example, at the end of 2 hours, 15 c.c. of complement might appear to be taken up, and next morning only ·05 c.c. It appeared, therefore, (*a*) that multiple doses of immune-body did not lead to the taking up of corresponding multiple doses of complement, and (*b*) that the complement taken up appeared to dissociate again in part, though this phenomenon might possibly be due to the presence of some complement molecules with very slow action. When, however, we used as the indicator *ox's corpuscles* treated with their corresponding immune-body, quite different results were obtained. The scheme is now :—

Guinea-pig's ○ + n IB + x rabbit's C : + Ox's ○ + IB.

The following results will serve as examples :—

Experiment LX.—1 D of IB took up 0.2 c.c. rabbit's C.
3 ,, ,, 0·45 ,, ,,
10 ,, ,, 1·16 ,, ,,

The M.H.D. of C was only 0·1 c.c. before the experiment; it is possible that it may have increased subsequently.

Experiment LXVIII.—2 D of IB took up 0·28 c.c. rabbit's C.
5 ,, ,, 0·58 ,, ,,
10 ,, ,, 0·74 ,, ,,

The M.H.D. of C was 0·06 c.c.

It is thus seen that when ox's corpuscles suitably treated are used as the indicator, the amount of complement taken up increases as the amount of immune-body is increased, though there is a greater deviation from strict arithmetical proportion than when guinea-pig's complement is used.

The difference in the results obtained with the two indicators (guinea-pig's and ox's corpuscles respectively), is manifestly due to the fact that there is in the rabbit's serum a complement which acts on guinea-pig's corpuscles, and not on ox's corpuscles, and that this complement either becomes dissociated from the guinea-pig's corpuscles or combines in very small amount. On the other hand the *chief* complement present acts on both varieties, and its union is a firm one;

even with this combination, however, the amount taken up appeared to diminish somewhat over night.

The fact already stated that, when guinea-pig's corpuscles were used as the indicator, additional doses of immune-body did not appear to lead to the taking-up of additional amounts of complement, raised the question whether there might not be two immune-bodies present, one of which acted with rabbit's complement, and one with guinea-pig's complement. Evidence of this was sought for by leaving the immune-serum in contact with the corpuscles for a time, then separating by centrifugalisation, and thereafter testing the dose of the uncombined immune-body with rabbit's and with guinea-pig's complement respectively. It is evident that if two immune-bodies were present, and were taken up by the corpuscles in different proportions, then the relative doses of the separated fluid would become changed. Such an investigation is theoretically of simple nature, but it is difficult to carry it out exactly, owing to the fact that it is not possible to remove completely the natural immune-body from the rabbit's serum, *i.e.*, to make this serum entirely devoid of hæmolytic action. In several experiments, however, allowance being made for this circumstance, it appeared that the relative doses with the two complements did alter in the way that the dose with guinea-pig's complement became relatively still higher, *i.e.*, after the contact with the corpuscles there seemed to be immune-body molecules left, which acted with rabbit's, but not with guinea-pig's complement. This may mean merely that the molecules of immune-body vary in their combining affinities, and that those with the weaker affinity act with the more powerful complement (rabbit's). The question is one of great complexity, and we have not attempted a full solution, as it did not appear necessary for the purposes of the present research. Everything goes to show, however, that the great majority of the immune-body molecules act both with rabbit's and with guinea-pig's complement; and we found that the presence of a small amount of guinea-pig's complement kept out of combination a certain amount of rabbit's complement, and *vice versâ*.

(c) *With Ox's Complement*—

The ox's complement is not a very suitable one to employ in this combination, as the natural serum of the ox has a very powerful hæmolytic action in itself, and it is only possible to remove a small proportion of the natural immune-body by contact experiments. Nevertheless, we have found that the dose of ox's complement, along with the immune-body to guinea-pig's corpuscles, is a small one, and there is no doubt that guinea-pig's corpuscles are very sensitive to the zymotoxic action of ox complement.

When we come to investigate the combining affinities, we find that multiple doses of immune-body have very little effect on the amount of ox's complement taken up, the amount taken up by means of from four to eight doses, for example, being very little more than that taken up by means of one dose. This may be due to a true want of combining affinity on the part of the complement, or it may be due to the combination being a very loose one. It may be noted, however, that there is practically no evidence of dissociation of complement in the course of 12 hours. The following will serve as an example :—

Experiment LXXIV.—1 D of IB took up 0·04 c.c. of ox's C.
4 „ „ 0·042 „ „
8 „ „ „ „ „

The indicator was guinea-pig's corpuscles treated with immune-body, for which the dose of ox's complement was 0·02 c.c.

II. Immune-body to Rabbit's Corpuscles (obtained by injecting the Guinea-pig).

(a) *With Rabbit's Complement.*—

This case is in many ways analogous to that of the immune-body to guinea-pig's corpuscles along with guinea-pig's complement. In both cases the hæmolytic dose of immune-body is ten times greater when the complement of the animal whose corpuscles are being tested is used, than when the complement of the other animal is used. This will be seen from the table. In this case, also, the dose of rabbit's complement is high, just as in the previous case the dose of guinea-pig's complement was. How much rabbit's complement is taken up when multiple doses of immune-body are used? The scheme of experiment is:—

Rabbit's ○ + n IB + x rabbit's C ⋮ + Ox's ○ + IB.

The following are some of the results:—

Experiment LXII.—1 D of IB takes up 0·14 c.c. rabbit's C.
10 „ „ 1·16 „ „

„ LXIII.—1 D of IB takes up 0·22 c.c. rabbit's C.
10 „ „ 1·12 „ „

„ LXVI.—1 D of IB takes up 0·086 c.c. rabbit's C.
5 „ „ 0·55 „ „
10 „ „ 0·9 „ „

Dose of rabbit's C with rabbit's corpuscles = 0·6 c.c. "1 D" = M.H.D. of IB along with guinea-pig's C. "10 D" = M.H.D. with rabbit's C (*vide* tables).

It will be seen that there is no lack of combining-power on the part of rabbit's complement, and that the amount increases with the amount of immune-body, though considerable deviations from exact arithmetical proportions are met with. Sometimes more, proportionally, is taken up by 10 hæmolytic doses than by 1 hæmolytic dose, sometimes less; we have met with the former phenomenon in several other experiments than that quoted, and are not able to give at present an explanation of it. Another point is that the hæmolytic dose of immune-body (expressed as "10 D. of IB.") leads to the taking up of more than a hæmolytic dose of rabbit's complement. This phenomenon is, probably, related to the fact brought out by Morgenroth and Sachs,[*] that the M.H.D. of complement sometimes varies greatly, according to the amount of immune-body used, and, conversely, the M.H.D. of immune-body may vary greatly, according to the amount of complement. The explanation of this is also outside the scope of the present paper.

(b) *With Guinea-Pig's Complement*—

The combination of guinea-pig's complement may be exemplified by the following:—

Experiment LXII.—	1 D of IB	took up	0·04 c.c.	guinea-pig's C.
	10 „	„	0·36 „	„
„ LXIII.—	1 D of IB	took up	0·012 c.c.	guinea-pig's C.
	10 „	„	0·27 „	„

The indicator was ox's corpuscles treated with immune-body. Here we have variations corresponding to those noted above.

We have also found that with this immune-body a small quantity of guinea-pig's complement keeps out of combination a certain amount of rabbit's complement, and that saturation with rabbit's complement implies practical saturation for guinea-pig's complement also. A similar statement applies to rabbit's complement keeping out guinea-pig's complement.

(c) *With Ox's Complement*—

Owing to the lack of serum, we have been unable to study the combining relationships of ox's complement through the medium of this immune-body. This defect, however, cannot modify the main conclusions arrived at.

III. Immune-body to Ox's Corpuscles (obtained by injecting the Rabbit).

It will be seen from the tables above that the dose of immune-body is practically the same with guinea-pig's as with rabbit's complement. The dose of the latter complement is the higher, and in a previous paper[†] it was shown that this was probably due to a smaller number of complement molecules in a given volume of serum, rather than to a weaker action of the zymotoxic group. The combining relationships of the two complements have also been fully discussed there, so that it is unnecessary to repeat the results obtained. It is sufficient to say that they behave as regards combination in hæmolysis pretty much as if they had the same haptophore groups. We shall refer merely to the action of ox's complement along with the above immune-body.

With this combination it is usually impossible to produce more than a fraction of lysis in the corpuscles (usually not more than a tenth), no

[*] Morgenroth and Sachs, 'Berlin. klin. Woch.,' 1902, No. 35.

[†] Muir and Browning, 'Roy. Soc. Proc.,' June 9, 1904.

matter how large amounts of immune-body and complement are used; in only one case did we get a considerable amount of lysis, about three-fourths. We never obtained complete lysis, however. In other words, the ox's serum does not "complement." Is this due to want of combining power of the ox's complement, or to the deficiency of toxic action? This question can be answered by finding the amount of complement taken up when varying amounts of immune-body are used. The scheme is:—

Ox's ○ + n IB + x ox's C : guinea-pig's ○ + IB.

As lysis does not occur in the first stage, the contents of each tube are centrifugalised, and the fluid is added to the guinea-pig's corpuscles. The following results were obtained:—

Experiment LXXIII.—1 D of IB took up 0·04 c.c. ox's C.
4 " " 0·05 " "
8 " " " " "

Dose of ox's complement for guinea-pig's corpuscles = 0·03 c.c.

Experiment LXXIV.—1 D of IB took up 0·014 c.c. ox's C.
4 " " 0·02 " "
8 " " " " "

Dose of ox's complement for guinea-pig's corpuscles = 0·02 c.c.

From these it is evident (1) that a considerable amount of ox's complement is taken up by one dose of immune-body (*i.e.*, by 1 M.H.D. as tested with rabbit's or guinea-pig's complement), but this amount of complement, which may be more than sufficient to produce complete lysis of rabbit's or guinea-pig's corpuscles, produces almost no lysis of the ox's corpuscles, and (2) the total amount of complement which can be taken up is almost reached with one dose of immune-body, additional doses of immune-body scarcely increasing the amount. There is, of course, in this case, no possibility of the phenomenon being due to dissociation of complement after combination, as the ox's corpuscles are removed by centrifugalisation before the guinea-pig's corpuscles are added, and, therefore, any complement obtainable must have been free in the fluid. Accordingly, we have here, again, an example of the relative non-sensitiveness of an animal's corpuscles to the action of its own complement when it is brought into union with them by an immune-body. But, in addition, there is, unlike the two previous cases, a deficiency also in the combining power of complement beyond a certain point, or, in other words, only a small proportion of the molecules of the red corpuscles combined with immune-body (R + IB molecules) take up ox's complement.

The fact that in the case just described, only some of the R + IB molecules take up complement is of considerable theoretical importance.

It is to be noted that almost all the R + IB molecules capable of taking up complement are present after the addition of one dose of immune-body, and that the subsequent addition of the same immune-body molecules scarcely increases the amount of complement taken up, though these molecules combine with the receptors of the red corpuscles. It would therefore appear that the failure on the part of an R + IB molecule to combine with complement, is due in some way to the receptors and not to the immune-body. According to Ehrlich's theory the amboceptor (immune-body) has practically no affinity for complement in the free state, but acquires that affinity when combined with the tissue or bacterial molecule. But the result above stated would, according to the amboceptor hypothesis, imply that only some molecules capable of combining with immune-body give the latter affinity for complement. According to the view that the immune-body renders the tissue molecule capable of taking up complement, the explanation would simply be that some of the molecules of the ox's corpuscles have no combining-group for the ox's complement, though they enter into combination with immune-body. It is not possible on theoretical grounds to establish either of these hypotheses by the exclusion of the other, but whichever may be ultimately established, the importance of the nature of the tissue molecule in determining whether complement will be taken up or not is brought out with sufficient clearness.

If we consider the action of guinea-pig's and rabbit's complements, it will appear that the striking variations in dosage brought out in the original tables, are due to the zymotoxic and not to the haptophore group. The combining relationships of the two complements may be compared in another way, viz., by adding a large amount of immune-body, say ten doses, and finding the ratio of rabbit's to guinea-pig's complement taken up in the case of the three sera. We have carried this out, and the following are the results. It was found most convenient to compare only two sera on the same day. Manifestly, only the two *ratios* in the same experiment are comparable.

				Ratio of two Cs.
Experiment LXX—				
Ox's corpuscles	10 D IB took up	0·44 c.c.	guinea-pig's C	1 : 1·27.
" "	" "	0·56 "	rabbit's C	
Guinea-pig's corpuscles..	" "	0·48 "	guinea-pig's C	1 : 1·17.
" " ..	" "	0·56 "	rabbit's C	
Experiment LXXI—				
Ox's corpuscles	10 D IB took up	0·18 c.c.	guinea-pig's C	1 : 2·6.
" "	" "	0·48 "	rabbit's C	
Guinea-pig's corpuscles..	" "	0·28 "	guinea-pig's C	1 : 2·1.
" " ..	" "	0·6 "	rabbit's C	
Experiment LXXII—				
Ox's corpuscles	10 D IB took up	0·26 c.c.	guinea-pig's C	1 : 1·4.
" "	" "	0·36 "	rabbit's C	
Rabbit's corpuscles.	" "	0·36 "	guinea-pig's C	1 : 1·4
" "	" "	0·54 "	rabbit's C	

It is thus seen that a comparatively close correspondence, considering the conditions of experiment, is brought out between the combining-ratios of the two complements in the case of these three sera.

The chief results may be summarised as follows :—

1. In the action of a complement there are two distinct factors, viz., (*a*) power of chemical combination, and (*b*) toxic action, corresponding to the "haptophore" and the "zymotoxic" groups of Ehrlich ; deficiency in the *action of complement (or in "complementing") does not necessarily* imply want of combining affinity, but may be entirely due to the non-sensitiveness of the tissue-molecule to the zymotoxic group.

2. In the case of the three hæmolytic sera studied the outstanding fact is the large dose both of immune-body and of complement necessary *when we use the complement of the same species of animal as that* whose corpuscles are being tested.

3. In all three cases there is a relative non-sensitiveness of the corpuscles of the animal to the zymotoxic group of its own complement; hence a large dose of immune-body is requisite to bring into combination the amount of complement necessary for hæmolysis. In one case (that of the ox) there is also a deficiency in the combining power of the complement with the receptors of the red corpuscles united to immune-body; from the two conditions acting together complete hæmolysis cannot be obtained.

4. Although differences among the molecules of the same immune-serum may occur, we have found no evidence that the striking differences in the dosage of the immune-body with different complements, and also in the dosage of various complements, are due to multiplicity of immune-bodies.

No one has yet succeeded in producing an anti-substance or immune-body by injecting an animal with its own corpuscles or cells—such a body as with the aid of complement would produce destruction of these cells. This is manifestly a provision against self-poisoning, and Ehrlich has applied to it the term *autotoxicus horror*. The results which we have brought forward, if they were found to hold generally, would go to show that even if some substance should appear which acted as an immune-body, there is a provision whereby the complement of an animal should produce comparatively little harmful effect.

"On the Presence of Tyrosinases in the Skins of some Pigmented Vertebrates.—Preliminary Note." By FLORENCE M. DURHAM. Communicated by W. BATESON, F.R.S. Received November 10,—Read December 1, 1904.

(From the Balfour Laboratory, Cambridge.)

In the course of an investigation of the "heredity of coat-colour in mice," the necessity for further knowledge, concerning the formation of pigment, became evident.

In the hairs of these animals, there are apparently three pigments (probably different forms of melanins), yellow, chocolate, and black. The characteristic colour of each mouse is due to the presence of one or more of these pigments. Thus, the yellow or "fawn" mouse has only yellow pigment in its hairs, the chocolate mouse has only the chocolate pigment, a black mouse has both chocolate and black pigments, while the house mouse or "agouti" mouse has all three pigments in its hairs (1).

The differences in the nature of these pigments have not been worked out as yet. Much work, however, has been done upon the origin of melanins and on their relationships to the aromatic decomposition products of proteids.

In 1901, v. Fürth and Schneider (2) showed that a tyrosinase could be obtained from the blood of certain insects. This tyrosinase acted upon a chromogen present in the blood, and converted it into a melanin-like substance. When a solution of tyrosin in water was treated with the ferment, a melanin-like body was also obtained. According to the observations of Przibram (which are published with those of v. Fürth and Schneider), a tyrosinase can be extracted from the ink-sac of *Sepia officinalis*. This ferment, acting in a like manner upon a watery solution of tyrosin, yields a black pigment, probably a melanin. Ducceschi (3) has shown that a similar ferment can be obtained from the blood of *Bombyx mori*.

Arguing from these facts, Cuénot (4), in a paper on the "Heredity of Coat-Colour in Mice," suggests that the formation of pigment in these animals is due to the presence, either of different chromogens and one ferment, or of two different ferments and one chromogen. The results of the action of the ferment on the chromogen would be to produce the characteristic colour of the mouse. The alteration of colour would be due either to the presence of a different chromogen, or to the presence of a different ferment.

It seemed worth while, therefore, to determine whether a ferment could be extracted from animals, which, like the mouse, are deeply pigmented in their coats; and to test whether, if such a ferment could be obtained from the skins of these animals, pigmented substances corresponding in colour to those of the animals taken, could be formed by the action of the ferment upon tyrosin or allied bodies.

I chose, for this purpose, the skins of young or fœtal animals, because these are in a condition of active pigment-formation. The study of adult forms shows that the older animals moult gradually, and that they would, therefore, in all probability, yield less material.

As young mice are very small, I preferred to use new-born rabbits and rats (of black or agouti origin) and fœtal guinea-pigs (about 8 weeks). In the case of the guinea-pigs, the skins of the mothers were also used for comparison.

The skins, having been removed from the animals, were chopped in a sausage-machine, and ground in an agate mortar with kieselguhr and distilled water. The use of this mortar was kindly permitted to me by Professor Sims Woodhead. The ground-up skins were then pressed out as completely as possible.

The expressed juice was red, and opaque in appearance. A portion of it was placed in a test-tube with solid tyrosin, and a milligram of ferrous sulphate was added as an activator. Toluol was then added as an antiseptic, and the tube was closed with cotton-wool, and placed in an incubator at 37° C.

For comparison, a series of tubes were prepared, in order to control the experiment. In the first tube boiled juice was placed, to which tyrosin and ferrous sulphate were added. In the second tube juice only was placed. The third tube contained juice, to which tyrosin was added. The fourth tube contained the juice, with a milligram of ferrous sulphate. The fifth tube contained no juice, but tyrosin in distilled water, with ferrous sulphate. These tubes were all placed in the incubator.

A similar series of tubes was also prepared, and kept at the ordinary temperature of the laboratory. A tube containing juice, tyrosin, and ferrous sulphate was also prepared, and kept at the laboratory temperature. In every case, toluol was used as an antiseptic. Cotton-wool was used to close the tubes, on account of the action of iron upon cork, which might introduce an error into the result.

In 24 hours, the contents of the tube, which was incubated, containing the juice, tyrosin, and ferrous sulphate showed a change in appearance. The fluid had darkened and a black substance was deposited; the amount of this substance increased as time went on. In no case did any of the other tubes arranged to control the experiment show any such change.

In one case, when considerable juice had been obtained from a number of young black rabbits, about 2 days old, a certain quantity of the juice was kept, in order to test the effect of time upon it. After it had been tested, it was kept standing for two days and fresh tubes were prepared from it. The blackening and formation of black substance occurred as before, but 48 hours in the incubator were required before the action commenced. The same juice was found to have lost its activity when kept for a week.

Experiments were then made with extracts of skins, which had been kept in alcohol (95 per cent.). The skins were chopped and ground with kieselguhr and distilled water, and pressed out as before. The resulting extract was colourless and cloudy in appearance. When treated with tyrosin and ferrous sulphate, and incubated, the same results were obtained, viz., darkening of the fluid and the formation of a black deposit. The time of action was delayed, so that about 10 days were necessary for the change of colour to appear.

I also tried the skins of black unhatched chickens, which had been kept in 95 per cent. alcohol, and obtained like results from them. The extract from the skins of the chickens was clear and colourless. After the darkening had commenced, I filtered the solution and added more tyrosin, and in this way, I was able to get a further deposit of black substance.

Solutions were prepared in another way. Juice, which had been obtained from the skins of fresh animals was saturated with ammonium sulphate. The resulting precipitate was filtered off, and was then washed with a solution of saturated ammonium sulphate, dissolved in distilled water and re-precipitated by saturation with ammonium sulphate. On re-dissolving this precipitate in distilled water, a certain portion of it was found to be insoluble. This was filtered off and the filtrate was dialysed against distilled water. When free from sulphate (as shown by testing with lead acetate solution), the clear, colourless fluid was treated with tyrosin and ferrous sulphate and incubated.

As before, pigment was formed, and as in the case of the skins preserved in alcohol, the action was delayed. About 10 days were required.

Amongst other animals tested in this way, I used self-coloured "red" guinea-pigs. I used the fœtal young and also the mother for comparison. The hair of this kind of guinea-pig contains only one pigment, deep yellow or orange in colour.

In the case of the young guinea-pigs, the solution became yellow and an orange-coloured deposit was formed. I filtered this off, and on the addition of more tyrosin, a fresh orange deposit was obtained. The extract made from the skin of the mother also changed in colour and yielded a yellow deposit, but less in amount than in the case of the young animals.

Hitherto, material from white or albino animals has yielded no results, but the animals obtained were too few for final conclusions to be formed in regard to them. Up to the present, only minute quantities of the coloured substances have been obtained, insufficient for complete analysis. They resemble melanins in being soluble in alkalis and insoluble in mineral acids. Further experiments are in progress, on a larger scale, to endeavour to produce enough for a thorough analysis.

Summary.

An extract can be made from the skins of certain pigmented animals (rabbits, rats, guinea-pigs and chickens), which will act upon tyrosin and produce a pigmented substance. This action suggests the presence of a tyrosinase in the skins of these animals.

The action of the tyrosinase is destroyed by boiling, does not take place in the cold, is delayed by time, requires a temperature of about 37° C., and also the presence of an activating substance such as ferrous sulphate to start it. [illegible]

The coloured substances produced are in accordance with the colour of the animals used. Black substances are obtained, when animals with black pigment in their skins are used, and yellow substance, when the skin contains the orange pigment. The coloured substances are soluble in alkalis, but insoluble in acids.

In conclusion, I take this opportunity to express my gratitude to Dr. Hopkins, to whom I am indebted for help and advice in the foregoing experiments.

LITERATURE.

(1) Bateson. 'Proceedings of the Zoological Society,' 1903.
(2) v. Fürth u. Schneider. 'Beitr. z. Chem., Phys., u. Path.,' Bd. 1.
(3) Ducceschi. 'Rendiconti della R. Accad. dei Lincei,' vol. 2.
'Archivio di Fisiologia,' vol. 1.
(4) Cuénot. 'Arch. d. Zool. Expér. et Gén., Notes et Revue,' vol. 1.

"On the Structure and Affinities of Fossil Plants from the Palæozoic Rocks.—V. On a New Type of Sphenophyllaceous Cone (*Sphenophyllum fertile*) from the Lower Coal-measures."

By D. H. Scott, M.A., Ph.D., F.R.S. Honorary Keeper of the Jodrell Laboratory, Royal Botanic Gardens, Kew. Received November 22,—Read December 1, 1904.

(Abstract.)

The class Sphenophyllales, of which the fossil described is a new representative, shows on the one hand clear affinities with the Equisetales, while on the other it approaches the Lycopods; some botanists have endeavoured to trace a relation to the Ferns. The nearest allies among recent plants are probably the Psilotaceæ, which some writers have even proposed to include in the Sphenophyllales.

The new strobilus appears to find its natural place in the type-genus *Sphenophyllum*, as at present constituted, but it possesses peculiar features of considerable importance, which may probably ultimately justify generic separation. The specimen, of which a number of transverse and longitudinal sections have been prepared by Mr. Lomax, is from one of the calcareous nodules of the Lower Coal-Measures of Lancashire, and was found at Shore Littleborough, a locality rich in petrified remains, now being opened up by the enterprise of the owner, Mr. W. H. Sutcliffe.

The close affinity of the strobilus with *Sphenophyllum* is shown by the anatomy of the axis, which has the solid triarch wood characteristic of that genus, and by the fact that the whorled sporophylls are divided into dorsal and ventral lobes, as in all other known fructifications of this class. But, whereas, in all the forms hitherto described, the lower or dorsal lobes are sterile, forming a system of protective bracts, while the ventral lobes alone bear the sporangia; in the new cone, dorsal and ventral lobes are alike fertile, and no sterile bracts are differentiated. On this ground the name *Sphenophyllum fertile* is proposed for the new species.

Each lobe of the sporophyll divided palmately into several segments, the sporangiophores, each of which consisted of a slender pedicel, terminating in a large peltate lamina, on which two pendulous sporangia were borne. In the bi-sporangiate character of the sporangiophores, and in other details of structure, *Sphenophyllum fertile* approaches the *Bowmanites Römeri* of Count Solms-Laubach, while in the form and segmentation of the sporophylls there is a considerable resemblance to the Lower Carboniferous genus *Cheirostrobus*.

The wall of the sporangium has a rather complex structure, the most interesting feature in which is the well-defined small-celled stomium, marking the line of longitudinal dehiscence.

The spores, so far as observed, are all of one kind; they are ellipsoidal in form, with longitudinal crests or ridges; their dimensions are 90—96 μ in length by 65—70 μ in width.

The most characteristic point in the structure of the new cone—the fertility of both dorsal and ventral lobes of the sporophyll—is regarded as more probably due to special modification than to the retention of a primitive condition.

"On the Convergence of Infinite Series of Analytic Functions."

By H. A. Webb, B.A., Fellow of Trinity College, Cambridge. Communicated by Professor A. R. Forsyth, Sc.D., LL.D., F.R.S.

Received November 10,—Read November 24, 1904.

(Abstract.)

Consider the differential equation

$$\frac{d^2y}{dz^2} + k^2 Qy = 0,$$

where

$$Q = Q_0 + \frac{Q_1}{k} + \frac{Q_2}{k^2} + \dots,$$

$\sqrt{Q_0}, Q_1, Q_2, \dots$, are one-valued analytic functions of z, independent of k, k is a constant, and the series defining Q is convergent for all values of k, such that

$$|k| > R,$$

except at the singularities of the functions

$$Q_0, Q_1, Q_2 \dots$$

Exclude points in the *z*-plane indefinitely near these singularities. The series

$$y = e^{ik\omega}\left(\phi_0 + \frac{\phi_1}{k} + \frac{\phi_2}{k^2} + \dots \textit{ ad inf.}\right)$$
$$+ e^{-ik\omega}\left(\psi_0 + \frac{\psi_1}{k} + \frac{\psi_2}{k^2} + \dots \textit{ ad inf.}\right),$$

where $\omega\ \phi\ \psi$ are functions of z independent of k, can be formally and uniquely constructed to represent any given particular integral of the differential equation.

For all values of z not excluded the series

$$\phi_0 + \frac{\phi_1}{k} + \frac{\phi_2}{k^2} + \dots, \qquad \psi_0 + \frac{\psi_1}{k} + \frac{\psi_2}{k^2} + \dots$$

are convergent, and when k is very large,

$$e^{ik\omega}\phi_0 + e^{-ik\omega}\psi_0$$

is an approximate value of the integral.

By means of this theorem approximate expressions for large values of one or more of the arguments can be found for many functions that occur in analysis and satisfy linear differential equations of the second order. For instance, the approximate solution of Lamé's equation

$$\frac{1}{y}\frac{d^2y}{dz^2} = n(n+1)\,k^2\mathrm{sn}^2 z + \mathrm{B}$$

for large values of n is

$$\mathrm{sn}^{-\frac{1}{2}} z\,[\mathrm{C}_1(\mathrm{dn}\,z + k\,\mathrm{cn}\,z)^{n+\frac{1}{2}} + \mathrm{C}_2(\mathrm{dn}\,z + k\,\mathrm{cn}\,z)^{-n-\frac{1}{2}}],$$

where C_1 and C_2 are arbitrary constants.

We can often determine the condition of convergence of an infinite series of functions by replacing the nth term by its approximate value for large values of n. For instance, the series of Lamé's functions*

$$\sum_{n=1}^{\infty} c_n \mathrm{E}_n^p(\sin x)\,.\,\mathrm{F}_n^p(\sin t),$$

where the c's are arbitrary constants, subject to the condition that the series

$$\sum_{n=1}^{\infty} c_n z^n$$

has unit radius of convergence, converges if

$$\frac{\mathrm{dn}(\xi, k)\,.\,\mathrm{dn}(\eta, k')}{\mathrm{cn}(\xi, k)} < \frac{\mathrm{dn}(\xi_1, k)\,.\,\mathrm{dn}(\eta_1, k')}{\mathrm{cn}(\xi_1, k)},$$

where

$$x \equiv \xi + i\eta, \qquad t \equiv \xi_1 + i\eta_1.$$

The limitation of the method is noteworthy; we cannot find the condition of convergence of the expansion of a given function in an infinite series of given functions without knowing—

(i) That the expansion formally exists; and

(ii) The approximate, if not the accurate, value of the nth term in the expansion for large values of n.

In the case of an expansion in hypergeometric functions, the limitation may be removed with the help of two theorems:—

(i) If $\phi(z)$ be a solution of the linear differential equation of the nth order,

$$(a_0 + a_1 z + \;.\;.\;.\; + a_n z^n)\frac{d^n y}{dz^n} + (b_0 + b_1 z + \;.\;.\;.\; + b_{n-1} z^{n-1})\frac{d^{n-1} y}{dz^{n-1}}$$
$$+ \;.\;.\;.\; + (k_0 + k_1 z)\frac{dy}{dz} + l_0 y = 0,$$

the coefficient of $\frac{d^r y}{dz^r}$ being a polynomial in z of order r; then

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* The notation is that of Byerly ('Fourier's Series and Spherical Harmonics,' p. 255 (1895)), $\mathrm{B} = p(1 + k^2)$.

$$f(z) = \int \frac{\phi(t)}{t-z} \cdot dt,$$

taken along a suitable path, satisfies the equation, and there are in general $(n-1)$ such integrals linearly independent.

(ii) If u and v be integrals of the equations

$$\phi_1(z)\frac{d^2u}{dz^2} + \phi_2(z)\frac{du}{dz} + \alpha\phi_3(z)\,u = 0,$$

and

$$\phi_1(z)\frac{d^2v}{dz^2} + \phi_2(z)\frac{dv}{dz} + \beta\phi_3(z)\,v = 0,$$

where ϕ_1, ϕ_2, ϕ_3 are any holomorphic functions of z, and α, β are two unequal constants, the integral

$$\int_{\mathrm{L}} uv\frac{\phi_3(z)}{\phi_1(z)} \cdot e^{\int \frac{\phi_3(z)}{\phi_1(z)} \cdot dz} \cdot dz$$

vanishes if L is a suitably chosen path.

We deduce the following result:—

Let $\phi(z)$ be any function of z which is regular at all points in the interior of an ellipse, C, whose foci are at the points $z = 0$ and $z = 1$. The ellipse passes through one (or more) of the singularities of $\phi(z)$. The curve is thus completely defined when $\phi(z)$ is given. Further, let p, q, γ be any constant quantities whatever, real or complex, save that neither $(p+1)$ nor γ is a negative integer. Then $\phi(z)$ can be expanded in the infinite series of hypergeometric functions.

$$\sum_{n=0}^{\infty} a_n \mathrm{F}(p+n, q-n, \gamma, z),$$

where

$$a_n = \frac{(p-q+2n) \,.\, \Pi(\gamma-q+n-1) \,.\, \Pi(p+n-1)}{\{\Pi(\gamma-1)\}^2 \,.\, \Pi(n-q) \,.\, \Pi(p-\gamma+n)}$$

$$\int^{(0+,\,1+,\,0-,\,1-)} t^{\gamma-1}(1-t)^{p+q-\gamma} \,.\, \mathrm{F}(p+n, q-n, \gamma, t) \,.\, \phi(t) \,.\, dt.$$

The series is convergent if z is inside C, and divergent if z is outside C; if z is on C the series is in general oscillatory and the expansion fails.

"Memoir on the Theory of the Partitions of Numbers. Part III."

By Major P. A. MacMahon, Sc.D., F.R.S. Received November 21,—Read December 8, 1904.

(Abstract.)

In this communication a "general magic square" is defined as consisting of n^2 numbers arranged in a square in such wise that each row, column, and diagonal contains a partition of the same number.

Such squares can be added together, by addition of corresponding numbers, without losing the magic property, and we can thus speak of a linear function of squares of the same order, the coefficients being integers. The squares can, in fact, be regarded as numerical magnitudes, and can be taken as the elements of a linear algebra. Since, moreover, arithmetical addition can be made to depend upon algebraical multiplication, the properties of the magnitudes can be investigated by means of a non-linear algebra.

The properties of a magic square can be exhibited by means of a system of homogeneous linear diophantine equations, so that it immediately follows that there is syzygetic theory of such formations.

The method of procedure is set forth and worked out in detail for the third order.

In Section 10 the general question of enumeration associated with a given sum is considered, and some particular results obtained.

The methods are applicable not only to general magic squares as herein defined, but to all cases of forms in "Arithmetic of Position," which retain their properties after addition of corresponding elements.

"Note on a Means of producing a High-voltage Continuous or 'Pertinacious' Current." By Sir OLIVER J. LODGE, F.R.S.

Received November 24,—Read December 8, 1894.

The methods hitherto employed for propelling a current through very high resistance have involved the use either of a very large static inductive machine, such as that of Wimshurst and others, or a battery of a very large number of cells, as employed by De la Rue, Trowbridge, etc. The author finds that by the use of high-tension mercury-rectifiers the same result can be attained with ordinary sources of supply, *e.g.*, by transforming and utilising the current from any steady or alternating main. In particular the use of rectifiers enables a high-tension intermittent or jerky current, such as that from a Ruhmkorff coil, to be trapped, and the supply stored in a couple of reservoirs, all the positive pulses in one, all the negative in another, whence they can be continuously discharged through any high resistance.

The author proposes to exhibit the effect at a forthcoming soirée. The arrangement was originally designed for the purpose of discharging large quantities of electricity into the air for the purpose of coagulating mist and fog.

"The Halogen Hydrides as Conducting Solvents.—Part III. The Transport Numbers. Preliminary Notice." By B. D. STEELE. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S. Received November 29,—Read December 15, 1904.

In continuation of this investigation[*] the transport numbers of several substances have been measured when dissolved in liquefied hydrogen bromide.

The substances selected were ethyl ether, acetone, methyl hexyl ketone and triethylammonium bromide, the first two of which have been shown to form compounds with hydrogen bromide.

As a preliminary to the main series of experiments the validity of Faraday's law for solutions in hydrogen bromide was tested, and the law found to hold within the limits of the errors of experiment of the method employed, which consisted in the direct comparison of the amount of hydrogen evolved during the electrolysis of various substances in hydrogen bromide solution, with the weight of silver deposited at the cathode of a silver voltameter.

In one experiment the amount of hydrogen evolved was 19·7 c.c., the hydrogen equivalent of the silver deposited being 19·8 c.c.

The transport numbers were determined by the method of Hittorf at a temperature of −81°.

Great difficulties were experienced in carrying out the analyses with the required degree of accuracy, and the method of analysis finally found to be successful was one depending on the direct weighing of the whole solution to be analysed in a specially constructed absorbing apparatus, and the subsequent determination of the hydrogen bromide by titration, the difference giving the amount of dissolved substance contained in the solution taken.

The following mean values were found for the transport number of the cation:—

Ether	$n = 1·0$,	$p = 0·82$
Triethylammonium bromide	$n = 0·5$ to $0·75$,	$p = 0·20$
	$n = 1·04$,	$p = 0·35$
Acetone	$n = 1·0$,	$p = 0·38$
	$n = 1·8$,	$p = 0·95$
Methyl hexylketone	$n = 0·9$,	$p = 0·39$
	$n = 1·8$,	$p = 0·77$

n = concentration expressed in gramme-molecules per litre.
p = cation transport number.

The experiments show that the cation transport number increases with increasing concentration, and that the ether (or acetone, &c.), functions as the cation or as a component part of it.

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[*] 'See 'Roy. Soc. Proc.,' vol. 73, pp. 450—455.

"The Halogen Hydrides as Conducting Solvents.—Part IV. Preliminary Notice." By B. D. STEELE, D. M'INTOSH, and E. H. ARCHIBALD. Communicated by SIR WILLIAM RAMSAY, K.C.B., F.R.S. Received November 29,—Read December 15, 1904.

Recent investigations have shown that the power of forming conducting solutions is manifested to a greater or less extent by a large number of inorganic and organic solvents. Some of the resulting solutions behave in a similar manner to those in water, as regards the variation with dilution of the molecular conductivity μ, and of the average molecular weight of the dissolved substance. Others show a variation of μ which appears to be inconsistent with Arrhenius' theory of ionic dissociation.

Conducting solutions in which the halogen hydrides and sulphuretted hydrogen act as solvents, are strikingly abnormal, and show, as has been pointed out in Parts 1 and 2,[*] an enormous diminution of μ with dilution, instead of the steady slow increase required by the theories of Arrhenius, Van't Hoff and Ostwald.

These abnormal results can, we believe, be simply explained on the assumption that the dissolved substance enters into combination with the solvent, and that the resulting compound undergoes ionic dissociation. It can be shown from the law of mass action that, if n molecules of solute combine with m molecules of the solvent to form a single molecule of the electrolyte, the concentration of the latter will be proportional to ν^{-n}, where $\nu^{-1} = c$ is the concentration of the original dissolved substance. But the specific conductivity κ is proportional to the number of ions, and this is proportional to the concentration of the electrolyte multiplied by α, where α is its coefficient of ionisation. Thus

$$\kappa = \alpha K c^n = \alpha K/\nu^2, \text{ if } n = 2,$$

or

$$\kappa\nu^2 = \alpha K.$$

If α varies but slightly over a given range this equation becomes

$$\kappa\nu^2 = K'.$$

It is found that the whole of our results may be thus explained. In some cases $\kappa\nu^2$ is approximately constant over a certain range of dilution; and that this approximate constancy does not hold at greater dilutions is to be assigned to the variation of α, which may become greater in more dilute solutions on account of a secondary dissociation intervening.

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[*] 'Roy. Soc. Proc.,' vol. 73, pp. 450 and 455.

This behaviour is manifested by, amongst others, a solution of hydrocyanic acid in hydrogen chloride, which gives the following values for ν and $\kappa\nu^2$.

$\nu =$	41·4	21·6	14·1	10·2	3·12	2·56	1·79	1·23
$\alpha K = \kappa\nu^2 =$	2·11	1·96	1·40	1·20	1·15	1·15	1·04	0·94

From these it will be seen that according to the foregoing explanation, α increases with dilution, a variation which is that required by the ionic theory.

In the case of triethylammonium chloride dissolved in hydrogen chloride α varies to a much greater extent, as the following figures show

$\nu =$	37·0	16·1	9·43	6·13	4·25	3·64
$\kappa\nu^2 = \alpha K =$	66·7	43·7	34·3	31·6	28·5	28·0

In both the foregoing cases n is found to be equal to 2, or two molecules of solute combine with the solvent to form the dissociating substance.

In other cases $n = 3$, or three molecules combine with the solvent, as for example, acetone dissolved in hydrogen bromide, for which solution

$\nu =$	8·33	5·00	3·23	1·64	1·35	1·07	0·75
$\kappa\nu^3 = \alpha\kappa =$	[7·00]	8·50	8·1	6·3	5·9	4·9	3·2

Here again the increase of α with dilution is clearly indicated.

For substances dissolved in water $n = 1$ and $K = \mu_\infty$, and since $\kappa\nu = \mu_\nu$ the equation $\kappa = \alpha K\nu^n$ becomes

$$\mu_\nu = \alpha\mu_\infty, \quad \text{or} \quad \alpha = \mu_\nu/\mu_\infty,$$

and for purposes of comparison with the foregoing the corresponding numbers for ν and $\kappa\nu$ are given for a salt. ($Cd\,SO_4$) dissolved in water.

$\nu =$	100	50	20	10	5	2	1
$\kappa\nu = \alpha K =$	71·8	61·8	49·6	42·4	36·2	29·1	23·8

Confirmation of these views is afforded by the results of the molecular weight determinations, which show that in many instances the molecular weight is greater than the normal, indicating that association has taken place to some extent.

"An Analysis of the Results from the Falmouth Magnetograms on 'Quiet' Days during the Twelve Years 1891 to 1902."

By CHARLES CHREE, Sc.D., LL.D., F.R.S., Superintendent of the Observatory Department of the National Physical Laboratory. Received November 23,—Read December 15, 1904.

(From the National Physical Laboratory.)

(Abstract.)

The paper contains an analysis and discussion of the results obtained from the declination and horizontal force magnetograms at Falmouth on quiet days from 1891, when the records commenced, until 1902. The discussion proceeds on parallel lines to those followed in dealing with the corresponding Kew* data for 1890 to 1900, and a comparison is instituted in many cases between Kew and Falmouth results.

The total secular changes of declination from 1891 to 1900 at Kew and Falmouth were identical, and the changes from year to year were closely alike. In horizontal force the annual changes recorded at the two stations did not agree so closely, and on the average the change at Falmouth was somewhat the greater.

When discussing the "non-cyclic effect" in the diurnal variation of the declination at Kew, it was pointed out that though so small and irregular as to be possibly attributable to accident, it yet presented features suggestive of a true physical origin. Though differences exist between the phenomena at Kew and Falmouth, still the points of agreement are such as to give strong support to the view that the phenomenon is not accidental.

The data considered being the means from the five selected quiet days a month, out of the 120 months in the 10 years 1891 to 1900 common to the two investigations, there is agreement of sign in the non-cyclic effects at Kew and Falmouth in 69 cases and disagreement in only 22, the effect being nil at one or both stations in the remaining 29 cases. Also at both places the sign of the non-cyclic effect, though prevailingly positive throughout the year, is distinctly negative near midsummer, and the seasonal variations in the two cases are fairly alike.

In horizontal force the non-cyclic effects at Kew and Falmouth are large and closely alike. From 1891 to 1900 there were only 5 months in which the non-cyclic effects differed in sign, as against 99 in which they agreed, and the mean values of the effects at the two stations differed by only about 5 per cent. of the mean value at Kew.

Whilst the mean daily range of temperature at Falmouth—a seaside station—is notably less than at Kew, the daily ranges of declination at

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* 'Phil. Trans.,' A, vol. 202, p. 335.

the two places are as nearly as possible equal, and the daily range of horizontal force is somewhat larger at Falmouth.

The annual variation of temperature range is again notably less at Falmouth than at Kew, the winter range at the former station being relatively high, and the summer range low. There is in this case a somewhat analogous state of matters in magnetics, the difference between the diurnal ranges at midsummer and midwinter being relatively less at Falmouth than at Kew, but the phenomenon is less marked than in temperature.

Analysing the diurnal inequality of temperature into harmonic terms of 24, 12 and 8-hour periods, General Strachey* found that the local time of occurrence of the maxima was distinctly earlier at Kew than at Falmouth, the difference being greatest for the 24-hour term, for which it amounted to nearly an hour. When the declination and horizontal force diurnal inequalities are similarly analysed, the local times of occurrence of the maxima are so nearly alike at the two stations that it is impossible to say with certainty which is the earlier. If a difference exists, it is of the order of only one or two minutes of time.

This last result applies to the average year of a sun-spot cycle. It has already been found that the time of occurrence of the first maximum in the 24, 12 and 8-hour terms at Kew varies with sun-spot frequency, being later in years when spots are numerous than when they are few. Thus the sun-spot maximum period 1892 to 1895, as compared to the sun-spot minimum period 1890, 1899 and 1900, showed a retardation of 15½ minutes in the time of occurrence of the maximum in the 24-hour term. The phenomena at Falmouth are closely similar, the retardation in the 24-hour wave in the period 1892 to 1895, as compared to the sun-spot minimum period 1899 to 1902, amounting to 14 minutes.

When the annual variations in the amplitudes of the daily ranges in declination and horizontal force at Kew, and of the 24, 12 and 8-hour terms in the diurnal inequality, were expressed as Fourier series, with an annual and a semi-annual term, there proved to be a remarkably close agreement between the dates of occurrence of maximum in the annual terms, and also in those of the semi-annual terms for the several elements. The same phenomenon appears at Falmouth, and there proves, moreover, to be a remarkably close agreement between corresponding Kew and Falmouth dates. Thus taking for both declination and horizontal force the three most important quantities considered, viz., the amplitudes of the diurnal ranges and of the 24-hour term in the diurnal inequality, and the sum of the 24 hourly differences from the mean for the day, and considering both the annual and semi-annual terms, we have 12 dates for the occurrence of the first maximum at

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* 'Phil. Trans.' for 1893.

Kew and at Falmouth. Of the differences between these 12 pairs of dates only three were as large as 2 days, and the mean of the differences taken algebraically was only about 2 hours. The agreement in short was well within the limits of probable error.

This result again applies to the average year of a sun-spot cycle. Comparing Falmouth results from the two periods, 1892 to 1895 and 1899 to 1902, it was found that a small but decided difference existed between the dates of occurrence of the maximum in the annual terms in both declination and horizontal force, and in the semi-annual term in declination. The dates proved to be *accelerated* in the sun-spot maximum period as compared to the sun-spot minimum period. To make certain that the result was not peculiar to Falmouth, a similar comparison was instituted between the Kew data for the two periods 1892 to 1895 and 1890, 1899 and 1900. The results were closely similar to those obtained at Falmouth. Thus the average results for the acceleration in the sun-spot maximum as compared to the sun-spot minimum period from the ranges, the 24 differences from the mean, and the 24-hour term in the diurnal inequality, were as follows:—

	Annual term.		Semi-annual term.
	Declination.	Horizontal force.	Declination.
Falmouth	3·5 days.	11·1 days.	6·4 days.
Kew..............	3·4 "	10·3 "	7·0 "

The phenomenon emphasises the importance of employing contemporaneous data when comparing two stations.

Applying Wolf's formula $R = a + bS$, associating the range R of a magnetic element with sun-spot frequency S, results are obtained for the variation of b and b/a throughout the year at Falmouth very similar in character to those previously obtained for Kew. On the whole the Falmouth values of b/a are distinctly the higher, *i.e.*, sun-spot influence is greater at Falmouth than at Kew.

Taking the above formula, but making S represent not merely Wolfer's sun-spot frequency, but in turn the areas of whole sun-spots, umbræ and faculæ as observed at Greenwich, Mauritius, and Dehra Dun, and given by the Astronomer Royal in the 'Monthly Notices of the Royal Astronomical Society,' values are calculated for a and b in the case when R represents the range of declination or horizontal force in the mean diurnal inequality for the year. A comparison is then instituted between the ranges for individual years of the 12-year period as calculated from the values of a and b thus found, and the Astronomer Royal's mean yearly data on the one hand, and as actually observed on the other. When S represents areas of whole sun-spots or of umbræ, the agreement between observed and calculated ranges is nearly though not quite as good, especially in horizontal force, as when S represents Wolfer's sun-spot frequencies; but when S represents areas of faculæ the agreement is much inferior, especially in years of sun-spot maximum. The mean differences between the ranges calculated from Wolfer's frequencies, and from either the spot areas or the umbræ is considerably less than between any one of the three sets of calculated ranges and the observed ranges. Also the differences between the observed ranges and those calculated from Wolfer's frequencies nearly always possess the same sign at Kew and Falmouth.

Both phenomena point to the conclusion that the differences between observed magnetic ranges at individual stations, and those calculated from any of the above measures of solar disturbance, though small, cannot be regarded as wholly fortuitous.

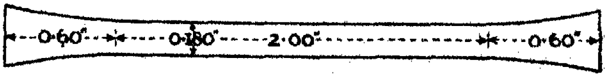
"The Effect of Liquid Air Temperatures on the Mechanical and other Properties of Iron and its Alloys."

By Sir JAMES DEWAR, F.R.S., Hon. M.I.C.E., and ROBERT ABBOTT HADFIELD, M.I.C.E., President elect Iron and Steel Institute.

Received November 24,—Read December 8, 1904.

As many iron alloys have shown anomalous results in their physical behaviour at ordinary temperatures, it became advisable to ascertain the exact effect of very low temperatures upon such bodies, and, accordingly, a series of tests were carried out on standard iron and iron alloyed with other elements, the specimens being selected from a large collection made by one of the authors, which is located at the Hecla Works, Sheffield. In the course of the enquiry some 500 specimens have been examined, and the detailed description of each test will appear later on in a special Monograph. In the meantime the more important results are submitted to the Royal Society.

For the purpose of the experiments, the irons were taken in the form of forged bars, and the iron alloys in the form of cast ingots 2¼ inches square. They were then carefully heated to the required forging temperatures and reduced to rods ¼-inch diameter, and from these rods finished test-bars 0·180 inch diameter were accurately machined to the following sketch:—



The bars were then forwarded to the Royal Institution Laboratory, and there tested in a small hydraulic testing machine, similar in principle to that described in 'Proceedings of the Royal Institution, 1894,' to which the necessary arrangements could be applied for breaking the specimens while immersed in liquid air.

The present research confirms, in a larger field, the conclusions set forth in the discourse of one of the authors at the Royal Institution in 1894 on the "Scientific Uses of Liquid Air," in which the results of tests on metallic wires and cast metals at low temperatures were discussed. The results of the present series of tests corroborate the inference previously drawn, viz., that all common metals and alloys increase in tenacity at low temperatures, and this whether the ductility increases or decreases, and, further, that the increase of tenacity is solely due to the low temperature, and persists only during its continuance.

The Results of Low Temperatures on Irons.—The first specimen examined in this class was Swedish charcoal iron, this material in its composition most nearly approaching that of pure iron. The analysis of this specimen gave C 0·045, Si 0·07, S 0·005, P 0·004, Mn trace, Fe 99·82 per cent. This iron, after careful annealing, gave 20 tons per square inch tenacity and 20 per cent. elongation at normal temperature; after cooling in liquid air the tenacity rose to 38 tons, with substantially no elongation. Another specimen, after being quenched at 950° C. and again at 600° C. in water, showed similar results in liquid air. Two other specimens in the unannealed condition and one after special heat treatment, showed similar properties. Specimens immersed in liquid air and allowed to return to the normal temperature before testing, showed almost exactly the same tenacity and elongation as before cooling, showing that the brittleness is entirely a function of temperature.

Several specimens were then quenched from 600° C., 800° C., and 950° C. in liquid air, and allowed to return to the normal temperature before testing. It might have been expected that with this extraordinary chilling a considerable hardening effect would have been noticed, but singular to say, whilst the tenacity is practically the same in each case, the ductility is improved rather than reduced. It may be mentioned that the specimens quenched from high temperatures in liquid air remained red hot in the liquid air much longer than would have been expected. In order to determine the hardness of these Swedish charcoal irons, a series of tests were carried out by the Brinell ball test, which showed that the hardness is increased nearly 200 per cent. by quenching in liquid air. The specimens, though, no doubt, much stiffer than at normal temperature, could be readily filed at − 182° C. Magnetic tests also showed that no marked change takes place at low temperature as regards this quality.

In order to determine whether there is a critical point where the abnormal rise in tenacity and loss of ductility occurred, four specimens were tested at + 18° C., – 80° C., – 100° C., and – 193° C. respectively. The results clearly show that there is no critical point, *i.e.*, gradual decrease in temperature is accompanied by gradual increase in tenacity.

Other irons tested were L.S.S. Swedish iron, English Bowling, and Cooke iron, all showing increase in tenacity and corresponding decrease in ductility upon quenching in liquid air.

The next class are *Iron-Carbon Alloys.* This class is of special interest and importance, as upon the various percentages of carbon present in steel depend chiefly its physical properties. The specimens first dealt with are those in which manganese is absent, or present in only very small quantities. Test No. 74 (C 0·14, Si 0·08, Mn 0·07 per cent.) represents very mild or soft steel; it enables a comparison to be drawn between the Swedish charcoal iron previously described and soft steel. In the case of this specimen the tenacity was nearly trebled, but it is apparently more ductile than Swedish charcoal iron. A specimen containing (C 0·78 per cent.) showed a considerable rise in tenacity in liquid air, the ductility being reduced to practically nil. A specimen of the same material was also submitted to the liquid air temperature, and allowed to return to normal temperature before testing; it showed a similar result to the original specimen not so treated. It may, therefore, be said that the effect produced by liquid air is of a physical and temporary character.

Other specimens, viz., Nos. 115 (C 0·83, Mn 0·25 per cent.), 9 (C 0·85, Mn 0·32 per cent.), 10 (C 1·09, Mn 0·32 per cent.), 13 (C 1·23, Mn 0·14 per cent.) showed the usual behaviour at liquid air temperature. Specimens of No. 115 (C 0·83 per cent.) were then quenched in liquid air from 700° C. and 750° C. respectively, and tested at normal temperature. As with the Swedish charcoal iron, the quenching from these comparatively high points has not produced the effect that might be expected; in fact, instead of the ductility being reduced, it is now quite considerable, viz., 13 per cent. from the 700° C. and 8 per cent. from the 750° C. Specimens of No. 13 (C 1·23 per cent.) also showed the same singular effects after quenching from 700° C. and 750° C. in liquid air. It is certainly most remarkable that a specimen containing 1¼ per cent. C., suddenly lowered 930° C., is so little injured as regards ductility. If these specimens had been quenched from the same condition in ordinary water or oil, they would have been unfileable and of extraordinary hardness. These specimens were as magnetic at – 182° C. as at normal temperature, and readily fileable.

In connection with this series, specimens were also taken of various iron-carbon alloys in which the Mn percentage was higher than in the preceding specimens, *e.g.*, Test Nos. 110 (C 0·19, Mn 0·52 per cent.), 1 (C 0·20, Mn 0·50 per cent.), 2 (C 0·50, Mn 1·00 per cent.), 3 (C 0·58, Mn 0·58 per cent.), 5 (C 0·75, Mn 1·00 per cent.), 11 (C 1·05, Mn 0·58 per cent.), 12 (C 1·20, Mn 0·62 per cent.), 31 (C 1·68, Mn 1·11 per cent.). All these specimens showed the usual rise in tenacity and fall in ductility, and although Specimen No. 31 is of abnormally high carbon, yet this does not appear to have interfered with the ordinary effect of the liquid air treatment. In the case of Test No. 1, after quenching specimens of the same material in liquid air from 700° C. and 750° C., the same peculiar behaviour was noticed as previously described, *i.e.*, considerable increase in ductility.

Having now dealt with the iron-carbon alloys, the various other alloys may be dealt with :—

Iron and Silicon	Specimens were tested representing all these alloys, but the results do not call for any special comment, the usual increase in tenacity and fall in ductility being noticeable at low temperature.
Iron and Aluminium	
Iron and Tungsten	
Iron and Chromium	
Iron and Copper	

Iron and Nickel.—Specimen No. 45 (C 0·26, Ni 0·58 per cent.). Although the liquid air doubles the tenacity, probably owing to the lower carbon and the presence of nickel, the elongation is not reduced to the extent noticed in previous specimens. This is important, and gives material proof that the brittleness of iron at low temperatures can be modified by another element, provided the carbon is not present in any considerable percentage. In another specimen, No. 46 (C 0·14, Ni 1·92 per cent.), the nickel appears to vigorously assert itself, as the ductility at − 182° C. only decreases from 20—12 per cent., the tenacity increasing from 34—59 tons. In Specimens Nos. 49 (C 0·19, Ni 3·82 per cent.) and 50 (C 0·18, Ni 11·39 per cent.), the remarkable effect of nickel is noticeable, as, whilst the tenacity rises considerably in both cases, the ductility remains practically unaltered. The tenacity rose in a further specimen, No. 54 (C 0·16, Ni 24·51 per cent.), in which the nickel is very high, from 90—118 tons at − 182° C., the ductility being only reduced from 12—10 per cent. The specimens were non-magnetic both at normal and at liquid air temperature. The same material showed an increase of from 306—524 in hardness under the liquid air treatment.

Iron and Manganese.—These form an important class. The peculiar alloy of iron and manganese, known as "Manganese Steel," is non-magnetic, and it is possible to produce similar alloys of iron and manganese even when the former element is present in as high a proportion as 87—88 per cent. Excellent results as regards physical properties can be obtained upon exceeding 1¼ and up to 2¼ per cent., provided the carbon is low. From about 3—7 per cent. the material is comparatively brittle, even with low carbon. Upon exceeding 7 per cent. the material now known as "Era" manganese steel is formed, and continues up to 17 or 18 per cent. Manganese steel proper is the alloy containing 11—15 per cent. of manganese with carbon varying from 0·80—1·40 per cent.

We will deal first with manganese steels having low carbon, *i.e.*, under 0·30 per cent. Test No. 14 (C 0·08, Mn 3·50 per cent.), the usual rise in tenacity and loss in ductility occurs at − 182° C., and on the specimen being allowed to return to normal temperature it does not appear to be injured in any way. Samples Nos. 15, 16, and 17 (Mn varying from 5·40—15·28 per cent.), which are extremely brittle at normal temperature, show very little modification at the low temperature.

Dealing now with alloys having higher percentages of carbon, several specimens tested with Mn ranging from 2·23 to 11·53 per cent. with carbon increasing proportionately from 0·41—1·66 per cent. showed normal behaviour at low temperature. An interesting specimen No. 26 (C 1·23, Mn 12·64 per cent.) was examined, representing a normal "Hadfield's Era manganese steel." At normal temperature this gave 56 tons tenacity, with the high elongation of 30 per cent., and after immersion in liquid air showed a slight rise in tenacity, the elongation, however, falling to 2½ per cent., the low temperature thus entirely de-toughening the material. This result is somewhat unexpected, as it might have been anticipated that the great ductility of this material at normal temperature would not have been interfered with to any great extent at the low temperature. In the ordinary treatment of Mn steel for toughening, the sudden drop in temperature is about 1000° C., and in the liquid air only 200° C. A repetition test, No. 26A, gave a similar result, the tenacity at normal temperature being 65 tons, with 40 per cent. elongation, while at − 182° C. the ductility dropped to nil, the tenacity remaining the same, viz., 64 tons.* Similar specimens of this steel cooled down and allowed to return to normal temperature again exhibited the usual extraordinary toughness of the material, thus showing that the de-toughening or embrittling action is only temporary, as with the Swedish charcoal iron and ordinary steel specimens.

It is certainly curious to find that a specimen of steel, which only a few moments before would break in the easiest manner, can again be bent double. This is produced by a change in temperature conditions of about 200° C. These results also show that manganese steel, notwithstanding its many peculiarities, in this respect falls into line with and is subject to the same laws as iron and ordinary steels. It is therefore all the more curious that the iron-nickel-manganese alloy (1414B) described later, entirely differs in this respect, where the effect of low temperature is not only nil, but there is a positive increase in ductility. The ball tests on specimen No. 26 shows an increase in hardness at −182° C. of 70 per cent., viz., from 205 to 372. Three other specimens, Nos. 26 E, F, and G are also interesting as showing the effect of quenching upon Mn steel, from temperatures of 605°, 800°, and 950° C. in liquid air, the tests being then carried out at normal temperatures. The specimens E and F give similar results to those that would be obtained by quenching in ordinary cold water at 600° and 800° C., *i.e.*, little or no increase in ductility. On the other hand, in specimen 26 G, quenched from 950° C., there is no doubt the result obtained, 66 tons tenacity *with 38 per cent. elongation, is excellent, but it is not any better than* can be obtained by quenching in water at 15° C. It is important to here mention that the three specimens E, F, G, were all non-magnetic at −182° C., showing that there is no change in the magnetic properties of manganese steel at low temperatures. This experiment finally settles quite a number of misunderstandings in metallurgical literature which have arisen on this subject, namely, that at no range of increase or decrease in temperature (provided this is not, as regards high temperature, sustained for any length of time) does any marked change in magnetic property occur in manganese steel.

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* It is very extraordinary that the metal iron, no matter what its treatment, never becomes so ductile as the treated and quenched manganese steel—mainly composed of iron—with an original ductility of 40 per cent.

The effect of low temperature on *Iron alloyed with Two other Main Elements.* Taking first the alloys of *Iron, Nickel,* and *Chromium.* Tests Nos. 78 (C 0·25, Cr 0·64, Ni 2·67 per cent.) and 81 (C 0·89, Cr 2·00, Ni 1·92 per cent.).—In the first instance in the presence of low carbon the nickel shows its toughening influence, as at −182° C. the tenacity rises from 38 to 61 tons, the elongation only falling from 20—17 per cent. In the latter specimen the effects of the nickel are not so apparent owing to the higher carbon, but the elongation does not entirely disappear. Another specimen of this latter material after quenching in oil at 760° C., and then water at 650° C. showed an increase in tenacity at −182° C. of from 81—105 tons, the elongation being, however, reduced from 7½ per cent. to nil. The embrittling influence of the carbon is seen in both instances. In the next specimen, No. 79 (C 0·31, Cr 1·80, Ni 2·60 per cent.), the ductility is not affected, remaining at 15 per cent. Notwithstanding the considerable presence of chromium, the nickel asserts itself in this specimen, the tenacity rising from 49—79 tons. A similar result was also noticeable in specimen No. 107 (C 0·17, Cr 1·55, Ni 3·02 per cent.), the tenacity rising to 59 tons, and the ductility dropping only from 25—20 per cent. Test No. 80 (C 0·64, Cr 2·01, Ni 12·24 per cent.).—In this specimen the very high tenacity at the normal temperature (115 tons) does not appear to be affected by the liquid air, in other words, a steel having high tenacity at normal temperature is practically unaffected by liquid air.

Iron, Nickel, and Silicon
Iron, Manganese, and Chromium
Iron, Manganese, and Silicon
Iron, Chromium, and Aluminium
Iron, Chromium, Silicon
Iron, Chromium, Copper
Iron, Chromium, and Tungsten

Tests were carried out in liquid air on specimens representing these alloys, but the results do not call for any special comment, in all cases the specimens behaving in the normal manner, *i.e.*, showing increase in tenacity and decrease in ductility in liquid air.

Iron, Manganese, Copper.—Test No. 19 (C 0·25, Mn 2·01, Cu 1·39 per cent.) shows a remarkable rise in tenacity, the elongation remaining unaffected by the low temperature. It is remarkable that the copper, which is present only to the extent of 1½ per cent., absolutely neutralises what would be the action of manganese, which clearly produces brittleness and hardness at low temperatures.

Iron, Cobalt, Manganese, Silicon
Iron, Chromium, Manganese, Silicon
Iron Nickel, Manganese, Aluminium

Tests were carried out on specimens representing these alloys, but the results do not call for any special comment.

Iron, Nickel, and Manganese.—In this class a number of specially interesting results were obtained. There is an important alloy, No. 1109D (C 0·60, Mn 5·04, Ni 14·55 per cent.), including two elements, which, if added separately in the same proportions to iron, would cause extreme brittleness. Most singular to say, this double combination now confers extraordinary toughness. This alloy is probably the most ductile form of iron alloy known, in several cases an elongation of no less than 75 per cent. having been obtained at normal temperature. Taking the first specimen, No. 60, under liquid air treatment, this material drops in elongation from 70—25 per cent., this remaining ductility even now being very great. This is the first specimen met with in which the ductility remains comparatively high. A further test carried out on the same steel shows a similar result. It may be mentioned that the magnetic qualities of the specimen remained unchanged at − 182° C. 1109D may be termed almost non-magnetic, though not so much so as manganese steel. 1109D is much more sensitive to magnetic changes by temperature, though to an ordinary magnetic test it appears inert.

The next specimen, No. 61 (C 1·00, Mn 6·05, Ni 17·91 per cent.), shows a further increase in nickel percentage, and this is clearly the factor in preventing loss of ductility at − 182° C., the ductility only decreasing from 57—42 per cent. Another specimen taken, No. 114

(C 1·18, Mn 6·05, Ni 24·30 per cent.) shows a still further increase in percentage of nickel. For the first time in this series of tests there is now met with a specimen in which there is an actual rise in ductility at − 182° C. The tenacity now rises from 51—84 tons, and the ductility from 60—to 67 per cent. This is remarkable. It is curious that the considerable percentage of manganese does not interfere with the toughening of the iron, of which there is 68 per cent. In any case it cannot be claimed that manganese confers this, as it must be remembered that a similar percentage of manganese in an iron alloy containing no nickel shows remarkable brittleness either at normal or low temperature. Nor does an iron alloy containing a similar high percentage of nickel and no manganese show much ductility. In face of these apparent anomalies it is difficult to offer a satisfactory explanation of the remarkable effects noticed. A repetition of the above test showed even more remarkable results, the ductility rising from 42—57 per cent.

The liquid air experiments on this series (iron, nickel, manganese) bring out in a much clearer manner than any other tests have yet done, the remarkable toughness and ductility of the iron alloys containing 6 per cent. Mn and 14—24 per cent. nickel. They show what an extraordinary molecular combination has been produced. In other words, these particular iron alloys have almost non-magnetic properties, possess the highest electrical resistance of any known alloy, and also represent the most ductile iron alloy yet known.

The Concluding Group includes Metals and Miscellaneous Alloys.—The first specimen taken in this group was No. 120 forged nickel (C 0·09, Ni 99·27 per cent.), representing an excellent quality of commercial nickel. This was tested in the forged condition, and in liquid air the tenacity was increased from 29—46 tons, and ductility from 43—51 per cent. This may be considered a remarkable result, and probably explains why in iron-nickel and iron-nickel-manganese alloys the presence of nickel (provided the carbon is low) prevents low temperature injuring iron. It is difficult to explain why this should be so, in view of the similar position of these two elements in the chemical classification of the elements.

Although no absolutely pure specimen of the metal manganese is yet available, that containing about 98 per cent. shows comparative brittleness, and in this respect, therefore, entirely differs from the metal nickel. This, to some extent, explains why nickel-iron alloys are remarkably tough, but still leaves unsolved why manganese steel, which contains 12 per cent. of Mn, is so extraordinarily tough when alloyed with iron and some carbon, and quenched from high temperatures.

Test No. 131 (copper 99 per cent.) shows that whilst the results obtained from this metal resemble nickel, the tenacity being increased, it is to a much less degree, the ductility not being materially altered.

It is curious to find that by chilling down the metals iron, nickel, and copper to − 182° C. their absolute and ultimate—if the terms may be allowed—qualities are shown more truly than at the normal temperature. The effects here noticed also explain in a more satisfactory manner than has yet been possible, why nickel is so valuable in nickel-iron alloys; that is, it tends to counteract the constant tendency of the sensitive metal, iron, to become embrittled on the slightest provocation. If this research reveals this one important fact, it will have well repaid the labour.

From the results it would seem to be indicated that copper might be a useful metal to alloy with iron. There are, however, difficulties in the way of this, at any rate as regards forged metal, as copper-iron alloys containing no manganese are considerably red-short, and cannot be readily manipulated. For some reason not yet explained it also does not alloy well with iron, but this may be a question of temperature effect at fusion point. At any rate, these experiments are suggestive for further research and investigation.

In the case of aluminium, Test No. 113 (Al 99·50 per cent.), the metal shows a remarkable increase in tenacity, viz., 8 to 15 tons, the elongation being nearly quadrupled, viz., from 7 to 27 per cent. Singularly enough, when alloyed with iron, such increases in both tenacity and ductility are not noticed; in fact, a contrary effect was produced.

Specimens of cupro-nickel (Cu 95, Ni 4·85 per cent.) and Bull's metal showed only slight changes at low temperature, whilst specimens of delta metal and manganese copper showed a rise in tenacity and ductility.

Various experiments carried out in connection with this research deal with contraction, electrical properties, micro-structure, magnetic and brittleness tests, all of which will be included in the special monograph.

General Conclusions.

It is clear that as regards iron and iron alloys, with, however, certain exceptions, the effect of low temperature is to increase in a remarkable degree their maximum tensile stress, and to reduce their ductility to practically nothing. These changes take place to the same extent, and this is very curious in the softest wrought iron, as represented by the specimens S.C.I. (Swedish charcoal iron), L.S.S. (the famous Swedish melting iron), and also English wrought iron, and in carbon steel samples from 0·10 to 0·20 per cent. to the high percentages, such as 1·25 or 1·50 per cent. Thus, the absence or presence of carbon in ordinary carbon steel, in which other special elements are not present, seems to have but little influence. That there is no error in this statement is proved, independently of the tensile tests, by the fact that several bars of the S.C.I., and mild steel specimens, were submitted to the low temperature test, and tested by hammer immediately after being immersed. In all cases they exhibited great brittleness, breaking off instantly upon being struck. Further confirmation is obtained by the Brinell hardness ball test, under which test the hardness number of the S.C.I. increased at − 182° C. from 90 to 266, or about equal to the hardness of 0·80 per cent. carbon steel at normal temperature. This almost seems incredible when it is remembered that the S.C.I. shows by analysis 99·88 per cent. of iron, and has only 20 to 22 tons tenacity, with 25·30 per cent. elongation.

The importance of the discovery of the toughening effect of nickel upon iron at low temperatures will be seen when it is understood that whilst it has been well known that nickel in certain percentages produced important improvements in the qualities and properties of iron and steel alloys, no microscopical or chemical research work has yet proved why this came about. It seems clear that these experiments go a long way towards offering a satisfactory explanation. The experiments prove that the purest iron, as represented by the S.C.I. (containing 99·82 per cent. iron), becomes brittle to an extraordinary degree under the influence of low temperatures, whereas nickel itself, tested under the same conditions, has improved rather than deteriorated, not only in tenacity, which iron also does, but in ductility, in which latter quality iron entirely breaks down. If nickel, therefore, is present in an iron alloy containing but little carbon, or comparatively low in that element, it acts as a preventive of brittleness, or is a very considerable modifier of that objectionable quality. It may be interesting to state that at ordinary temperatures the toughness or ductility of nickel is no greater than that of iron. For example, in comparative tensile tests made on nickel and pure iron, the ductility of iron was greater.

Iron to a more or less degree, at any rate in manufacturing operations, always seems to be endeavouring to wander out of the "paths" of ductility and toughness, and will assume its apparently brittle nature on the slightest provocation. It would appear therefore that iron, a cheap and convenient metal itself, must be permeated by some element that will mask or modify its properties. Until recently carbon was the only element known to modify the properties of iron; but, as will be seen in this research, this element, where great toughness is required, only helps to make matters worse. Fortunately for iron, however, its close companion nickel acts as a preventive in keeping it from wandering out of the narrow road of metallurgical rectitude, that is toughness or ductility. Why this should be so cannot at present be explained. Iron is a crystalline metal, whereas nickel appears to be much more amorphous; it is possible, therefore, that nickel tends to prevent iron crystallizing. This action of nickel is remarkable in certain of the alloy specimens, *e.g.*, No. 114, which is an alloy of iron, carbon 1·18 per cent., nickel 24·30 per cent., and manganese 6·05 per cent. Here the ductility is extraordinary at not only normal but low temperatures, probably the highest known for any iron alloy, and certainly for an alloy having such tenacity as 85 tons per square inch. There is still present in this alloy 68 per cent. of iron, yet the tendency of the latter metal to become brittle is not only entirely checked at the low temperature; but the elongation, already so great, is considerably increased, viz., from 60 to 67½ per cent. There is also an increase of tenacity in both cases, viz., a rise from 10 to 38 per cent. Thus the nickel present causes the bar under high tension, and at − 182° C., to remain far more ductile than the very best ductile iron of one third the tenacity. Although the action of nickel has been specially referred to, it must not be overlooked that in this alloy there is also present 6 per cent. of manganese, which in its ordinary combination with iron, that is with no nickel present, would confer intense brittleness upon the iron and render it more brittle than if not present. This treble combination of nickel, manganese, and iron, appears to reverse all the known laws of iron alloys.

We have to thank the mechanician of the Davy-Faraday Laboratory, Mr. C. N. Cooke, for able assistance in the conduct of the experiments.

"The Effects of Temperature and Pressure on the Thermal Conductivities of Bodies. Part I.—The Effect of Temperature on the Thermal Conductivities of some Electrical Insulators."

By Charles H. Lees, D.Sc. Communicated by Arthur Schuster, F.R.S. Received November 29,—Read December 15, 1904.

[Abstract.]

The substance whose thermal conductivity is to be determined has the form of a cylinder about 8 cms. long, 2 cms. diameter, and is surrounded by a thin cylinder of brass, which on account of its comparatively high thermal conductivity, makes the outer surfaces of the substance isothermal surfaces. The brass cylinder is placed in a Dewar tube.

The heat is supplied by the passage of an electrical current through a platinoid wire embedded in the substance parallel to the axis of the cylinder, and about ·4 cm. distant from it. The amount of heat generated is determined by the current through the wire and the potential difference between its ends. The temperature is measured by the electrical resistance of two short spirals of No. 40 pure platinum wire, down the centre of one of which the heating wire passes. To eliminate errors due to want of symmetry, a second heating wire passes down the centre of the second spiral, and the heating current may be sent through either or both at will.

The difference of temperature of the two spirals is determined by making them two arms of a resistance bridge, the other two arms of which are equal. By means of mercury cups resistances may be placed in series with either of the spirals till a balance is obtained. From the resistance necessary to effect the balance and the "fundamental constants" of the platinum thermometers which the two spirals constitute, the difference of their temperatures is calculated. The thermal conductivity k of the medium would, if the latter were infinite in extent and the heating wire infinitely long, be connected with the difference of the temperatures v_1, v_2 at the two points distant r_1 and r_2 from the heating wire, and the amount of heat H generated per second in 1 cm. of the latter, by the equation

$$v_1 - v_2 = \frac{H}{2\pi k}\log\frac{r_2}{r_1}.$$

In the apparatus used the connection between the quantities is not so simple, but the theory is worked out completely in the paper, and the corresponding expression given.

The following fairly representative substances have been tested each at a number of temperatures between that of liquid air and the melting point of the substance: Ice, glycerine, aniline, paraffin wax, naphthaline, β-naphthol, para-nitrophenol, and diphenylamine.

The results show a marked increase of the conductivities of ice, naphthaline, aniline and nitrophenol, and a slight increase of those of β-naphthol, and diphenylamine at low temperatures. Glycerine has a maximum conductivity about −80° C., and paraffin wax shows a tendency to behave in the same way.

A few values of the conductivities for a portion of the range of temperature are given in the following table:—

	At 120° abs.	At 180° abs.	At 240° abs.	Previous values.
Ice	0·0062	0·0058	0·0052	0·00568, Neumann, 'Ann. Ch. Phys.,' vol. 3, p. 66. 0·0050, Mitchell, 'Roy. Soc. Edin. Proc,' vol. 86, p. 592. 0·0014 liquid at 20° C.
Naphthaline......	0·0013	0·0011	0·00091	0·00096 at 33° C., Lees, 'Phil. Trans.,' A, vol. 191, p. 416.
Aniline	0·0011	0·00086	0·00070	0·00041 liquid at 12°, H. F. Weber, 'Berl. Ber.,' 1885.
Nitrophenol (para)	0·0010	3·00085	0·00070	
Glycerine	0·00078	0·00082	0·00076	0·00062 liquid at 13° C., Graetz., 'Ann. der Phys.,' vol. 25, p. 337. 0·00067 liquid at 12° C., H. F. Weber, *loc. cit.* 0·00068 liquid at 25° C., Lees, *loc. cit.*
Paraffin wax	0·00060	0·00065	0·00061	0·00061 at 35° C., Lees, 'Phil. Trans.,' A, vol. 183, p. 481.
β-Naphthol	0·00067	0·00065	0·00063	0·00081 at 32° C., Lees, 'Phil. Trans.,' A, vol. 191, p. 416.
Diphenylamine ...	0·00058	0·00054	0·00052	

The temperatures are given in terms of the hydrogen scale, measured from the absolute zero, the thermal conductivities in c.g.s. units.

It will be noticed that the thermal conductivities are much greater in the solid than in the liquid state in the case of water and aniline, but almost alike in the case of glycerine.

"On the Normal Series satisfying Linear Differential Equations."

By E. Cunningham. Communicated by Dr. H. F. Baker, F.R.S.

Received December 8,—Read December 15, 1904.

(Abstract).

If y denotes a column of n elements, and u is a square matrix of n rows and columns of elements, each of which is a function of the independent variable, n independent solutions of the system of simultaneous equations

$$dy/dt = uy$$

are given by the n columns of the matrix

$$\Omega(u) = 1 + \mathrm{Q}u + \mathrm{Q}(u\mathrm{Q}u) + \mathrm{Q}\{u\mathrm{Q}(u\mathrm{Q}u)\} + \ldots . ;$$

where $\mathrm{Q}(\phi)$ denotes $\int_{t_0}^{t} \phi \, dt$.

In the 'Proceedings of the London Mathematical Society,' vol. 35, pp. 333 ff., the form of this solution is developed by Dr. H. F. Baker, for the particular case in which each element of u has a pole of order unity at the point $t = 0$. This is the case of a system derived from a linear ordinary equation of order n, all of whose integrals are regular in the neighbourhood of $t = 0$.

If χ is any square matrix of order n, and η a square matrix satisfying the system of equations

$$d\eta/dt = u\eta - \eta\chi,$$

then $y = \eta\Omega(\chi)$ is a matrix satisfying

$$dy/dt = uy.$$

This result is used by Dr. Baker in the paper above mentioned to show that in the above case a solution may be found in the form $\eta\Omega(\chi)$, where the elements of η are simply series of powers of t, and the matrix $\Omega(\chi)$ is expressible in finite terms. The form of the result puts in evidence what are known as Hamburger's sub-groups of integrals.

The present paper deals with the linear system of equations in which the matrix u is of the form

$$\frac{\alpha_{p+1}}{t^{p+1}} + \frac{\alpha_p}{t^p} + \ldots . + \alpha_0 + \beta_1 t + \ldots .,$$

α_r, β_r being matrices of constants.

The general linear ordinary equation of order n which has $t = 0$ as a pole of its coefficients is reduced to this form. It is shewn, in the first place, that provided the roots of the determinantal equation

$| a_{p+1} - \theta | = 0$ are all different, a matrix χ can be found, of the form

$$\frac{\chi_{p+1}}{t^{p+1}} + \frac{\chi_p}{t^p} + \ldots + \frac{\chi_1}{t},$$

in which all elements of χ_r, save the diagonal elements, are zero, such that the system of equations

$$d\eta/dt = u\eta - \eta\chi$$

is formally satisfied by a square matrix whose elements are series of positive integral powers of t, generally divergent.

The elements of the matrix $y = \eta\Omega(\chi)$ are therefore of the form

$$e^{\frac{\theta_{p+1}}{t^p} + \frac{\theta_p}{t^{p-1}} + \ldots + \frac{\theta_2}{t}} t^{\theta_1} \{c_0 + c_1 t + c_2 t^2 + \ldots\}.$$

Secondly it is found that, if the roots of the equation $| a_{p+1} - \theta | = 0$ are not all unequal, provided certain conditions attached to each group of equal roots are satisfied, a matrix

$$\chi = \frac{\chi_{p+1}}{t^{p+1}} + \ldots + \frac{\chi_1}{t}$$

can be found, having all elements to the left of the diagonal zero, such that the equations

$$d\eta/dt = u\eta - \eta\chi$$

are still formally satisfied by a matrix of series of positive integral powers of t.

The matrix $\Omega(\chi)$ can, in this case also, be completely integrated in finite terms; the result may contain a certain number of powers of $\log(t)$.

Applied to the single linear equation of order n it is seen that the n integrals fall into groups of the form :—

$$e^{\frac{\theta_{p+1}}{t^p} + \frac{\theta_p}{t^{p-1}} + \ldots} t^{\theta_1} \{\phi_0 + \phi_1 \log(x) + \ldots + \phi_r (\log x)^r\}.$$

Lastly, when the conditions above mentioned are not satisfied, the system of equations is transformed by the change of variable $t = z^k$ to a new system of the same type in which the coefficients have poles of order k_{p+1} at $z = 0$.

It is then shown that in all cases an integer k can be found, such that the conditions that the new system can be solved by expressions of the above form are all satisfied.

The groups of *subnormal* integrals thus found agree with those obtained by Fabry* directly from the linear equation of order n.

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* Thèse, 1885, Paris.

"The Flow of Water through Pipes.—Experiments on Stream-line Motion and the Measurement of Critical Velocity." By H. T. Barnes, D.Sc., Assistant Professor of Physics, and E. G. Coker, M.A., D.Sc., Associate Professor of Civil Engineering, McGill University. Communicated by Professor Osborne Reynolds, F.R.S. Received November 4,—Read November 24, 1904.

In a brief note published in the 'Physical Review,'* we have described a thermal method of observing the change from stream-line to eddy motion for water flowing through pipes of different diameters. This method we have recently employed in a series of experiments, which we have carried out on a much larger scale than was previously attempted. The method had several points to recommend it for our particular work, the chief one being the simplicity of the experimental arrangements. The object in undertaking this investigation, for which our method was adapted, was in the interest attached to a study of stream-line flow, where every form of initial disturbance was as completely removed from the water as possible.

The impossibility of heating a column of water uniformly throughout while flowing in stream-line motion has been previously observed.† It was shown that, when water is heated electrically while flowing through a tube of two or three millimetres in diameter by a central wire conductor, the heat is carried off by the rapidly moving stream, which forms a cloak of hot water around the wire, and leaves the walls of the tube almost entirely unheated. If the heat be applied to the outside of the tube, the heated water remains in contact with the inner surface of the tube and the water flows through the centre of the tube at a much lower temperature. It is quite different if the flow is increased sufficiently to break up the stream-lines. In this case, eddy or sinuous motion results, and the distribution of heat throughout the water column becomes uniform.

The change from stream-line to eddy motion can be very clearly observed in a tube heated on the outside, since the temperature of the emerging stream immediately increases when the flow rises above the critical point. The point of change is very sharp, and the disappearance of the stream-lines instantaneous.

At the outset of our work we were guided by the two very important papers of Osborne Reynolds,‡ in which the laws governing the flow of water in pipes and channels are worked out. It is clear from a study of the work of Reynolds that the change from stream-line to eddy motion may take place within a wide range of velocities. We may observe the critical velocity in two ways: either by observing the velocity at which the stream-lines break up into eddies, or by obtaining the velocity at which the eddies from initially disturbed water do not become smoothed out into stream-lines in a long uniform pipe. The first change may be at any velocity within certain limits depending on the initial steadiness of the inflowing water, while in the second, the change can take place at only one velocity. It therefore depends on whether we start with initially quiet water or disturbed water what value will be attained. Below what we will call the lower limit of critical velocity or stream-line flow, the stream-lines will form the stable flow whatever may be the condition of the water before entering the pipe. If it be in a disturbed state, a short length of pipe is required before the eddies are smoothed out, but stream-lines finally appear further on and subsequently persist as the stable flow. The greater the initial disturbance in the water, the greater will be the length of pipe probably required before the eddies disappear. The flow at which the eddies persist throughout the entire pipe, however long, indicates that the change has taken place from one kind of flow to the other. This point of change is the true critical velocity, and although the production of eddies at the mouth of the pipe may vary, it will be independent of them. If the initial disturbance, however, is not sufficient to prevent the water from starting in stream-line motion, the critical velocity is raised. The change in flow in this case takes place by the birth of eddies in the pipe itself, and the point of change is in some way related to or limited by the degree of steadiness in the water. In regard to this point, Reynolds says, on p. 955 of his original memoir: "The fact that the steady motion breaks down suddenly shows that the fluid is in a state of instability for disturbances of the magnitude which cause it to break down. But the fact that in some conditions it will break down for a large disturbance, while it is stable for a small disturbance, shows that there is a certain residual stability so long as the disturbances do not exceed a given amount.

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* 'Physical Review,' vol. 12, p. 372 (1901).

† H. T. Barnes, 'Phil. Trans.,' A, vol. 199, p. 234 (1902).

‡ 'Phil. Trans., 1882 and 1895.

"The only idea that I had formed before commencing the experiments was that at some critical velocity the motion must become unstable, so that any disturbance from perfectly steady motion would result in eddies.

"I had not been able to form any idea as to any particular form of disturbance being necessary. But experience having shown the impossibility of obtaining absolutely steady motion, I had not doubted but that appearance of eddies would be almost simultaneous with the condition of instability. I had not, therefore, considered the disturbances except to try and diminish them as much as possible. I had expected to see the eddies make their appearance as the velocity increased, at first in a slow or feeble manner, indicating that the water was but slightly unstable. And it was a matter of surprise to me to see the sudden force with which the eddies sprang into existence, showing a highly unstable condition to have existed at the time the steady motion broke down."

In this connection it is a matter of interest to note that when all forms of initial disturbance, as well as the disturbing influence of the walls of the pipe, are removed, eddy motion is no longer possible. Such a condition of affairs we have in a jet of water issuing from a circular orifice. It is easy to show experimentally that the beautiful rod-like appearance of the water jet depends on the absolute quietness of the water feeding the jet, and that the jet is immediately broken up by producing eddies artificially. Jets flowing in stream-line motion at a speed of from 20—30 feet per second have been obtained by us from a two-inch orifice.

In our present series of experiments we arranged that our pipes should feed from the same tank from which we produced the jets, in order that we might be sure to have the water in a perfectly quiet state. We could, therefore, be fairly safe in assuming that the birth of eddies was the result of the disturbing influence of the walls of the tube only.

Two methods of study were adopted by Reynolds in his experiments. The first was the method of colour bands, which gave the point at which stream-lines break up into eddies, and which we have called the upper limit of critical velocity, and the second was a method of pressures, where the relation between velocity and pressure was obtained above and below the critical velocity. In the colour-band tests a long narrow tank was used, in which the pipe was placed. A flare, carefully smoothed, was fastened to the inflow end, while the outflow end protruded out of the tank and connected with the waste pipe. A small tube containing coloured liquid was directed just in front of the flare and a thin stream of colour was drawn into the tube with the water. This thread of colour remained intact all along the tube for stream-line motion, but disappeared with great suddenness when the critical velocity was reached. The water in the tank was allowed to become as quiet as possible before beginning the experiment. The rate of flow was calculated from the rate of lowering of the water surface, and the dimensions of the pipe. In the pressure experiments the water was allowed to flow directly from the mains into the pipe. After a sufficient length of pipe to allow of the dying out of the eddies, pressure gauges were attached at a fixed distance apart, and readings of velocity and pressure made. The critical velocity was not observed directly by this method, but since the resistance changes with the change in the flow, from the first power of the velocity to about the

1·7th power, the intersection of the logarithmic homologues gave a method of determining it. Reynolds remarks that for a short distance above and below the critical velocity the gauges became unsteady and no readings could be made.

By means of his experiments Reynolds was able to verify his mathematical deductions, and he showed from three different pipes, together with a comparison with the experiments of D'Arcy for large pipes and with Poiseuille's for small tubes, that the critical velocity varied inversely as the diameter of the pipe. He further showed that the critical velocity followed the viscosity temperature law as deduced by Poiseuille, and, therefore, varied as the viscosity over the density. Similar experiments with three different pipes by the method of colour bands showed that the upper limit followed the same laws approximately. The theoretical equations, however, had to do with the lower limit.

In our experiments on the upper limit of critical velocity with absolutely quiet water, we found that stream-lines were preserved in many cases to very much higher velocities than would be expected from the inverse-diameter law, and that the upper limit falls off slightly more rapidly with rise in temperature than the law of Poiseuille. We do not wish to lay stress on these points, or intimate in any way that we think they question the validity of the theoretical laws which have been so completely worked out by Reynolds. We think, however, that they show the instability of the upper limit of stream-line flow, and how much it depends on forms of disturbance. We have, moreover, made independent determinations of the temperature variation of the lower limit, and find by two different methods that over a wide range in temperature the critical velocity follows the viscosity temperature law accurately.*

The slight deviation from the theoretical law for the variation with temperature of the upper limit which we have observed in the case of two pipes of different diameters is, we think, due to the fact that it becomes more and more difficult, as the temperature rises, to maintain stream-line flow in the unstable region. This would result in the upper limit apparently falling off more rapidly than the temperature formula would allow for.

The question has suggested itself to us that some form of initial disturbance in our tank may have come in as the temperature was raised to cause a greater falling-off in the upper limit than the theoretical. Convection currents might have supplied such a form of disturbance, but the size of our tank and the fact that the mouth of our pipes was always placed at or near the middle, together with the length of time required for the tank to cool down, make it appear to us improbable that convection currents played an important part.

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* E. G. Coker and S. B. Clement, 'Phil. Trans.,' A, vol. 201, p. 45 (1903); H. T. Barnes, 'B. A. Report,' Belfast (1902).

Thermal Method of Measuring Critical Velocity.

In some of our first experiments, we observed the change in temperature in the column of water at the critical velocity by noting the increase in resistance of a platinum wire threaded through the centre of the tube, which was heated on the outside, and our preliminary results showed that the presence of a wire of 6 mils. thickness in a tube of ½ inch in diameter was quite sufficient for our purpose. We found that the point of change in flow could be observed more simply by placing the bulb of a mercury thermometer in the stream of water as it flowed out of the tube. A glass prolongation, of slightly greater diameter and connected carefully to the brass pipe by a specially constructed cone or adapter, enabled the readings on the thermometer to be observed. It was a matter of interest to us to see the sudden way in which the reading on the thermometer indicated the point of change by an almost instantaneous change of reading.

We were fortunate in having at our disposal, through the kindness of Dr. H. T. Bovey, F.R.S., the facilities offered by the hydraulic laboratory, where the large experimental tank, 20 feet high and 25 square feet in area, served admirably for a reservoir. The tank stood on the bed-rock, and was therefore free from disturbance in the rest of the building, and, after the eddies occasioned by filling had died out, the water was in a very quiet state. The water used for the experiments was supplied from the Montreal mains and was quite clear; and every precaution was taken, by repeated cleaning, to have the water and tank clean. The action of finely divided matter in suspension in the water is to cause a breaking-up of the stream-lines, so that it was necessary for us to avoid this form of instability.

Our preliminary experiments, made to test the method before applying it on a large scale, were quite satisfactory, and, after profiting by various trials, the final apparatus took the form of that represented in fig. 1.

In one side of the large tank A, a hole was cut, in which was fitted a special form of stuffing box to take the tubes of different sizes. Each tube was made of brass and joined to a metal trumpet flare, such that the inside was filed perfectly smooth, and free from sharp points which might disturb the flow. The flare was located at about the centre of the tank, so as to be as free as possible from convection streams along the sides of the tank when working at high temperatures. The end of the pipe protruding from the tank was inserted in a cylindrical water jacket B, with ends closed by stuffing boxes similar to those on the tank. From the end of the tank a glass prolongation C held the mercury thermometer placed and securely fastened centrally in the tube. The glass tube was cemented into a brass tube, connected with a screw-down valve D, for regulating the flow. From the valve a pipe led to a two-way switch over E, provided with one pipe to waste and one pipe leading to the double-coned copper measure, shown at F. This measure had been very carefully calibrated by Mr. T. P. Strickland some time previously.

For small flows, where the time for filling the tank became inconveniently long, a smaller vessel was used and the amount of discharge obtained by weighing on a large bullion balance. For the high temperature experiments, a worm pipe G was inserted in the outflow so as to cool the water before it entered the measure. Water was circulated continuously through the jacket by means of a centrifugal pump H, operated by a Pelton water motor I. A gas flame J, under the pump, served to regulate the temperature of the jacket. A thermometer K was placed in the water circuit so that the temperature could be regulated at will and maintained a few degrees above or below the temperature of the water flowing out from the tank. A graduated disc L was provided on the valve, by means of which a pointer on the valve gave an indication of the amount opened.

During the greater part of the experiments, the temperature of the tank was taken from a long-stem thermometer placed so that its bulb reached to the centre somewhat below the flare on the pipe. It was found that the temperature thus indicated differed but little from the stream-line reading on the thermometer in the glass prolongation at high temperatures, and was in practical agreement with it at the lower points. For the majority of the experiments, an average head of about 8 feet was maintained, sometimes running down to 4 feet, but seldom getting as low as that. One filling of the copper measure only lowered the head $\frac{3}{4}$ of an inch, so that no constant level device was necessary. The temperature of the tank could be raised to any point up to 90° C. by means of a steam heater. A stirrer was also fitted to the tank, but of course was not kept moving after the temperature of the tank was once brought to a uniform state.

The method of making an experiment was very simple. One observer stood at the valve and regulated the flow until it was seen by the reading that the stream-lines had completely disappeared, and the other observer then switched over the flow into the measure and took periodic readings of the temperatures. The time was taken on a chronograph during the earlier runs, but was changed to a Frodsham and Keen chronometer which had been carefully rated. The water in the tank was always allowed to remain undisturbed for several hours before taking an experiment. For the high temperature experiments the tank was heated to about 90° and then allowed to settle. Over a

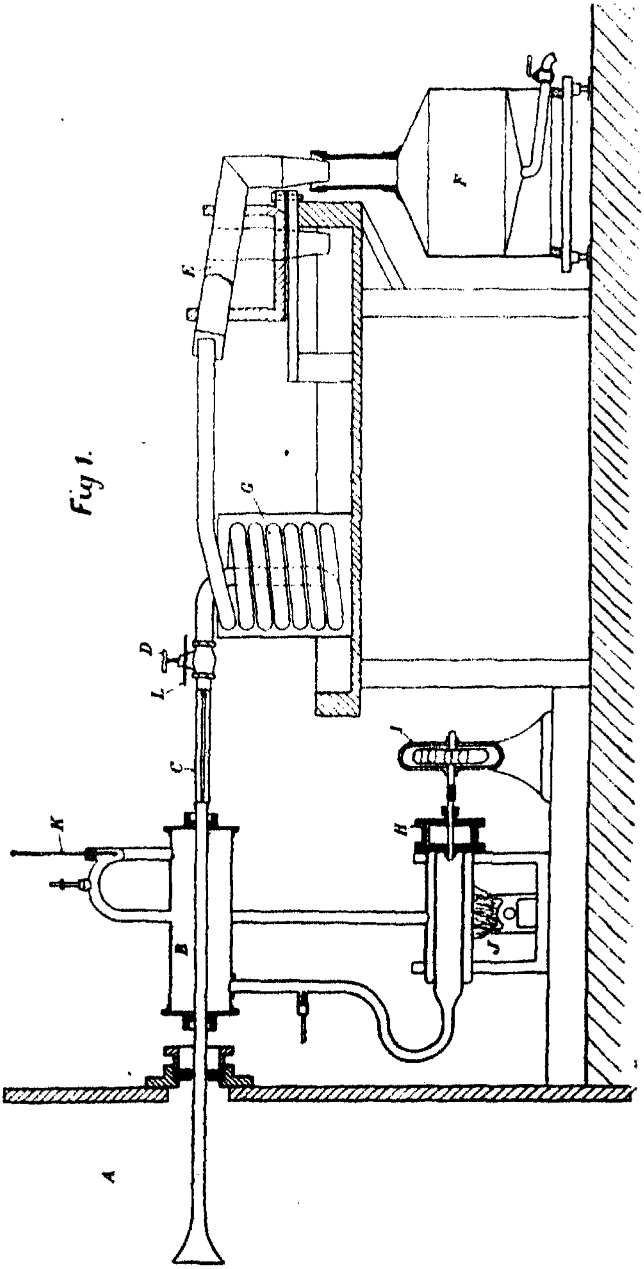

Fig 1.

week was required for the tank to cool down, during which time successive readings were made. No two determinations were ever made with one setting of the valve, but in every case a re-determination of the critical velocity was made.

It might be questioned whether the presence of the thermometer bulb in the outflowing stream could have produced a disturbing influence, but in no case was the bulb placed inside the tube under test. We think that our very high values obtained in many cases for the critical velocity show conclusively that the bulb had no influence, and especially in the tubes we used, which were all considerably larger than the thermometer bulb.

In order to satisfy ourselves on many points in connection with our measurements, we made some tests to determine the effect of a change of length on the critical velocity. To do this we first took a pipe 3·6 metres long and 1·95 cm. in diameter, and determined the critical velocity by moving the temperature jacket to the end where the glass prolongation began. We obtained the following readings:—

	Temp.	V_c in ft. per sec.	V_c in metres per sec.
	16·0	3·79	1·155
	16·0	3·82	1·163
	16·1	3·66	1·115
	16·1	3·92	1·192
Mean......	16·05	3·80	1·158

The tube was then removed and cut in the middle, so as to be only 1·8 metres long, and the following readings were obtained:—

	Temp.	V_c in ft. per sec.	V_c in metres per sec.
	15·4	3·66	1·115
	16·7	3·84	1·170
	16·7	3·82	1·163
Mean......	16·2	3·77	1·148

The agreement is really better than the individual observations. For each of these readings the flow was closed off and then opened carefully until the jump took place on the thermometer. The readings could have been repeated to any desired accuracy of course by leaving the flow unchanged.

The formula for calculating the critical velocity which Reynolds deduced from his experiments for the upper limit reads:—

$$V_c = \frac{1}{43 \cdot 7} \frac{P}{D},$$

where D is the diameter of the pipe in metres, and P is a function of the temperature, which was found to be the formula obtained by Poiseuille for the change in flow of water in capillary tubes.

P then equals

$$(1 + 0{\cdot}03368\,T + 0{\cdot}000221\,T^2)^{-1}.$$

Calculating the upper limit for this pipe we find:

$$V_c = \frac{0{\cdot}0228}{0{\cdot}0195 \times 1{\cdot}59} = 0{\cdot}734.$$

This value comes out 0·734 metre per second instead of 1·15, as we observed it. The higher limit obtained in our measurements is undoubtedly due to the steadiness of the water at the mouth of our pipe.

We convinced ourselves in these experiments that we had not exceeded the upper limit, for the valve controlling the flow was moved very slowly as the point was reached, and stopped instantly the jump took place. It was possible to obtain the stream-lines again by slightly closing the valve. For a velocity of 0·7 metre we had perfectly steady stream-lines. For our smaller pipe, 1·05 cm. in diameter, we found a close agreement with the formula of Reynolds, but that above this, for pipes of larger diameters, the deviations became larger the larger the pipe.

If we tried the experiments too soon after filling the tank, before the water had become perfectly steady, the upper limit came much lower, and, as the water became more settled, a higher limit was indicated by a tendency to form stream-lines, followed by a breaking-up, giving rise to the phenomenon described by Reynolds as "flashing." The flashes became less frequent until, finally, the water being perfectly steady, the higher limit was reached. It was possible to obtain the higher limit as soon as the flashes started, since it was only necessary to increase the flow until the flashing ceased. The flashes showed themselves by an oscillation on the thread of the thermometer.

It was not, therefore, really necessary to have absolutely quiet water to obtain the upper limit, since we were able to satisfy ourselves by experiment that the flashes indicated a disturbance in the tank, which, if removed, would enable us to reach the upper point without their appearance at all. Hence, flashing was taken to indicate a tendency to form stream-lines, and if they appeared, the upper limit was obtained by increasing the flow until the permanent reading on the thermometer indicated that eddy motion was the steady flow.

Stream-Line Flow at High Velocities.

The 1·8 metre length of our brass pipe had remained attached to the tank for several days under an 8-foot head, after completing our experiments, to test the influence of length. On returning to this pipe, we not only passed our former limit, but were unable to make the stream-lines break up until we produced an artificial disturbance by giving the pipe a sharp rap. The change in flow produced by the jar was seen by the jump on the thermometer reading. It returned to the stream-line reading as soon as the rapping ceased. We, unfortunately, did not measure the flow in this case, but we at least doubled the previous value of 1·148 metres per second. Being somewhat surprised by this result, we made some experiments on this same pipe by colour bands, instead of the thermometer, in order to satisfy ourselves that the high values we obtained were not due to some peculiarity of the thermal method. After some trouble we introduced the colour tube into the tank, and dispensed with the heating jacket. For this we were obliged to let the water out of the tank, and introduce fresh water. Owing to the disturbance thus caused, it was several days before we could proceed with the experiments. It was a simpler matter than we had supposed to observe the colour band, since we had removed the thermometer from the glass prolongation, the thread of colour could be distinctly seen issuing from the brass pipe. We obtained, in these experiments, a critical velocity at the same point as before, but, on opening the valve, the stream-lines re-formed at higher velocities, and persisted to the highest velocity we could produce. This corresponded with our thermal results, except that, in this case, we had an actual re-formation of stream-lines at the higher velocities after eddies had appeared at the usual point.

In order to study the re-formation of the stream-lines more easily, a glass pipe, specially made for critical velocity experiments, with a flare blown on to the tube, was inserted, and a colour tube was put in as before. The tube was 1·2 metres long, and 1·47 cms. in diameter. No thermometer was used, or heating jacket, and the head was about 8 feet, as before. We found, incidentally, that by increasing the quantity of colour it was possible to cause a very large disturbance in the flow.

The following readings were obtained:—

	Temp.	V_c in feet per sec.	V_c in metres per sec.
Little colour ………	20° C.	3·466	1·056
,, ,, ………	20	3·366	1·026
Excess of colour ……	20	1·252	0·382
Little colour ………	19	3·786	1·154

These observations showed the importance of using little colour, as a small colour stream produced practically no effect.

Working out the value of V_c as before from the formula, we get at 20° C. the value 0·88 metre per second. This value is, again, much less than the observed value using little colour.

We observed that by opening the valve, and increasing the flow, the stream-lines appeared to re-form. This was shown by a return of the thread of colour. It was not until we reached a velocity of 2·97 metres per second that the thread again disappeared. By altering the flow a little at this point we could make the thread of colour disappear, or obtain it clearly defined. We repeated this several times, and found that the definite nature of this point was remarkable, the thread of colour appearing in almost as sudden a manner as it disappeared.

The diameter of the pipe plays an important part in obtaining the higher stream-line flow, for we found that with a pipe 1·05 cms. in diameter we could not pass the upper limit, nor cause a re-formation of stream-lines. We made some experiments with a brass-pipe, 5·41 cms. in diameter, and 1·5 metres long, by the method of colour bands, and found that we could carry the stream-line flow up to velocities of 1 metre per second, which was the highest flow we could measure. To obtain this flow we were obliged to arrange a much larger measure to handle the water discharged. The upper limit for a pipe of this size, according to the formula, amounts to about 0·24 metre per second at 20° C. We, therefore, exceeded this by four times, as far as we could see, without the formation of eddies. There was a tendency to flash at the highest point, but no definite critical velocity, and the thread of colour could be seen very distinctly.

We cannot enter into a discussion of the influence of the diameter of the pipe on the attainment of the second stream-line flow, but it appears to us obvious that we were able to obtain these higher readings only by paying the strictest attention to the steadiness of the water in the tank. The magnitude of our tank, and the volume of water at our disposal, made this comparatively easy. The inverse diameter law has been shown by Reynolds to be true both for the upper and lower limits, and our experiments show the same where the water has not become perfectly steady; but it is probable that, as the diameter of the pipe becomes larger, the disturbing influence of the walls becomes less effective in causing a breaking up of the stream-lines. In the jet experiments, where there is no directing pipe, stream-line is the stable flow for all velocities, providing the water has become absolutely quiet. For pipes of small diameter, under ½ inch, or 1 cm., the steadiness of the water probably becomes less important, compared with the influence of the walls of the pipe. It is probable that for absolutely quiet water the inverse diameter law holds up to 1 cm., beyond which the critical velocity apparently increases with increasing diameter, until for large pipes we approach the jet. The higher critical velocity may be a second critical velocity, but we have not decided this point.

Temperature Effect on the Upper Limit by the Thermal Method.

In Table I we give the series of experiment obtained for the effect of temperature on the upper limit for our smallest brass pipe, 1·05 cms. in diameter. The results are worked out for each point, correcting the volume of the water in the measure to the volume at the temperature of efflux from the tank. The velocity of efflux was then calculated in the usual manner. In fig. 2 we give a plot of the observations, which extended from 15°—86°. Unfortunately, we were unable to extend below 15°, on account of the temperature of the water in the mains not being below that at the outset of the experiments. During the time of the experiments, June and July, after the beginning of the hot weather, the temperature steadily rose in the mains to as high as 20°, where it stayed during the remainder of the work.

Table I.

D = 0·0105 metre.

Temperature.	Total quantity in cubic inches.	Total time in seconds.	V_C in metres per second.
20°·2	3910·7	644·2	1·146
40·1	3898·7	1085·4	0·677
34·1	3891·8	929·9	0·789
29·1	3894·5	811·4	0·905
23·6	3897·9	675·8	1·088
22·8	3895·6	674·3	1·091
56·6	3918·7	1753·0	0·421
49·1	3908·8	1592·7	0·466
84·3	1781·8	245·1	0·137
72·9	1778·1	129·6	0·259
47·3	3893·8	1442·0	0·512
23·3	3899·4	675·5	1·091
20·2	3903·8	643·8	1·149
15·09	3902·9	525·7	1·401

In Table II we give Reynolds' observations for his two smaller pipes, the diameters of which lie just above and below our pipe. These tests were made with colour bands. In the last column we reduce the observations to a pipe equal in area to ours, by the simple ratio of the diameters. In the plot we have included Reynolds' observations, and indicated them by circled crosses. We have, also, included the temperature law of Poiseuille.

Table II.—Reynolds' Observations on Pipes 2 and 3 reduced to a Pipe 1·05 cm. in diameter.

Temperature.	V_c in metres per sec.	Temperature.	V_c in metres per sec.
22°	1·086	6°	1·849
11	1·478	6	1·869
11	1·489	6	1·838
11	1·505	6	1·957
11	1·528	6	1·978
11	1·556	4	1·981
		4	1·891
		4	2·027

In the next table we give a summary of the observations which we obtain for our larger brass pipe at various temperatures.

Table III.

Temperature.	V in feet per sec.	V in metres per sec.
21°·3	3·458	1·054
34·5	2·059	0·628
40·0	1·791	0·546
51·0	1·362	0·415
55·0	1·115	0·340
70·8	0·631	0·192
73·6	0·777	0·237

These results are plotted in Fig. 2 and represented by circled dots. The general slope of the two curves is the same and, although the agreement between the different determinations is not perfect, it is sufficient to show that the upper limit falls off more rapidly than the theoretical law.

The temperature variation of the upper limit may, from these observations, be represented by the formula

$$P = (1 + 0{\cdot}0300\,T + 0{\cdot}000704\,T^2).$$

We do not think that the divergence indicates a temperature variation for the critical velocity different to the theoretical, but rather that it shows, as we have pointed out in a previous part of this paper, that the true critical velocity is at the lower limit. The inverse diameter law does not hold for our larger pipe, as will be seen by reference to the plot, and we have shown that it does not hold for the upper limit in the case of our other large pipes.

Temperature Variation of the Lower Limit.[*]

In a note by one of the authors (H. T. B.), read before the Belfast meeting of the British Association, it was announced that the thermal method had been applied to the measurement of the lower limit of stream-line flow, and that, from measurements at different temperatures, it had been found that the variation with temperature followed the theoretical accurately.

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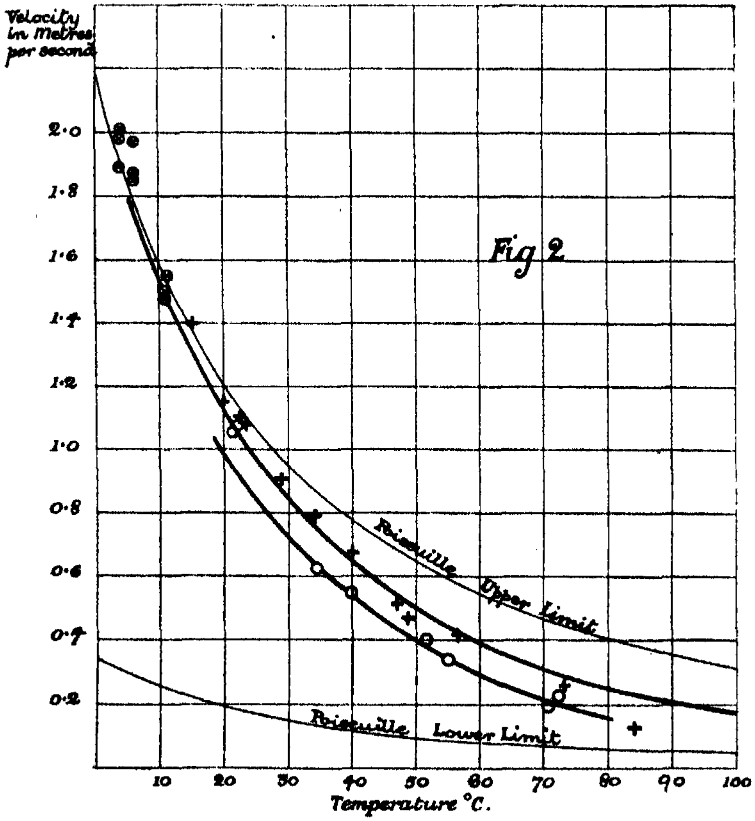
[*] Compare also E. G. Coker and S. B. Clement, *loc. cit.*



The thermal experiments were arranged in the following way:—A large copper tank was fitted with a lead pipe, 8 feet long, coiled up in a smooth spiral. One end of the pipe was connected with the water mains, and the other protruded from the side of the tank and passed through a water-bath, 2 feet long, the temperature of which could be regulated at will and maintained constant by a special form of continuous electrical regulator. The pipe was fitted with a glass prolongation, similar to our previous experiments, and a thermometer was used as before. The tank was fitted with an electrical heater, by means of which the temperature could be changed quickly at will and maintained constant. For the low temperature experiments, an ice-and-water mixture was placed in the tank.

It was found that it was possible to measure three flows: that at which the flow was entirely stream-line with no tendency to form eddies; second, that at which the eddies remained in the flow without the appearance of stream-lines; and third, that at which the eddies and stream-lines followed each other at regular intervals. The change from one flow to the other was observed by the rate of the oscillation on the thread of the thermometer. An inspection of the curves given by Reynolds for the relation between velocity and pressure, above and below the critical velocity, shows that no sharp line of intersection exists between the curve representing stream-line and that representing eddy motion, but that there is a portion over a considerable range of flow where the readings are unsteady. It was in this region that the three flows mentioned above were found. The first was the highest limit of the stable stream-line, the second the lowest limit of the stable eddy flow, and the third the point half-way between. The results are given in the following table for the third point, which is the critical velocity of Reynolds:—

Table IV.

Diameter of pipe, 0·0125 metre.

Temp.	Q. c.c.	Time. secs.	V_c.	P.	UL.
6°	830	30·2	0·225	0·238	0·239
6	866	30·2	0·234	0·238	0·239
17·2	952	45·2	0·171	0·176	0·167
17·2	930	45·0			
18·1	951	45·1			
18·1	926	45·2			
18·1	944	45·1	0·171	0·172	0·163
18·1	960	45·0			
18·1	923	45·2			
40·5	580	45·3			
40·5	568	45·2	0·103	0·104	0·086
40·5	565	45·1			

The first column contains the temperature at which the critical velocity was measured. The second column contains the total quantity of liquid Q which was collected in the measuring glass during the time given in the third column. The times were all taken on a stop-watch. Under V_c are given the values of the critical velocity, calculated in the usual way from the area of the pipe and the flow per second. Under P the values of the critical velocity are given, calculated by Reynolds' lower-limit formula. This formula reads—

$$V_c = \frac{1}{278} \cdot \frac{P}{D}$$

in metres per second, where P and D have the same meaning as before.

In the last column, UL, the values of V_c are given, calculated by the same formula, but using for P the temperature variation deduced from the experiments on the upper limit. The correspondence of columns 4 and 5, and the divergence in column 6, are quite sufficient to show that the temperature variation of the lower limit is in agreement with the law of viscosity rather than with the formula obtained from the upper limit. The experiments are important in showing a close agreement with the theoretical formula of Reynolds, which requires not only the viscosity formula to hold, but the inverse-diameter law as well. The agreement of the individual observations confirms our previous conclusions, in showing the uncertainty in measuring critical velocity, not from the want of accuracy in the measuring appliances, but from the variation in the point itself. It is only by taking a mean of a number of observations that anything like an accurate value can be obtained.

"The *Rôle* of Diffusion during Catalysis by Colloidal Metals and Similar Substances."

By Henry J. S. Sand, Ph.D., M.Sc., University College, Nottingham. Communicated by Professor J. H. Poynting, F.R.S.

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In a paper on reaction-velocities in heterogeneous systems, Nernst[*] has recently put forward the view that all chemical reactions taking place on the boundary of two phases proceed to equilibrium practically instantaneously, and that the velocities actually observed are simply those with which diffusion and convection renew the reacting material at the boundary. As a special instance of heterogeneous reactions, he mentions catalytic decompositions due to finely divided particles, such as colloidal metals, and he believes it probable that the kinetics of these reactions can be deduced from the assumption that chemical equilibrium remains permanently established on the surface of the particles.

Processes of this kind have recently undergone a considerable amount of experimental investigation, the most important instances being the catalytic decomposition of hydrogen peroxide due to colloidal platinum[†] and colloidal gold[‡] by Bredig and his pupils, and the catalytic decomposition of the same substance due to hæmase by Senter.[§] In his last paper Senter discusses his reaction in the light of Nernst's hypothesis, and arrives at the conclusion that the known facts do not contradict it.

[*] 'Ztschft. Phys. Chem.,' vol. 47, p. 52 (1904).

[†] Bredig and Müller, v. Berneck, 'Ztschft. Phys. Chem.,' vol. 31, p. 258 (1899); Bredig and Ikeda, *ibid.*, vol, 37, p. 1 (1901).

[‡] Bredig and Reinders, 'Ztschft. Phys. Chem.,' vol. 37, p. 328 (1901).

[§] *Ibid.*, vol. 44, p. 257 (1903); 'Roy. Soc. Proc.,' vol. 74, p. 201 (1904).

With regard to this result, it must be observed that a colloidal solution of hæmase does not afford the most suitable example from which to draw theoretical conclusions, as nothing whatever is known regarding the size of the active particles, their nature and their number. More definite results can be obtained from a criticism of Bredig's experiments, for in them we are dealing with platinum, or gold, substances of known properties, the absolute quantities of which are stated for every experiment. Moreover, although we are without definite information regarding the shape, size, and number of the particles, yet we are safe in assuming that in those colloidal solutions which were at all stable, no particles occurred of a diameter greater than $0{\cdot}5\,\mu$.* In order to carry out any calculations, the diffusion coefficient of hydrogen peroxide is also requisite. So far as I am aware, this number has not been determined. If we take as representative of diffusion coefficients of non-electrolytes at 25°, the following values determined by Scheffer for molecules heavier than that of hydrogen peroxide :—

Urea, $0{\cdot}94\,[1 + (25^\circ - 7{\cdot}5^\circ)\,0{\cdot}025]\,10^{-5} = 1{\cdot}35 \times 10^{-5}\,cm^2/\text{sec.}$;
Chloral hydrate, $0{\cdot}64\,[1 + (25^\circ - 9^\circ)\,0{\cdot}025]\,10^{-5} = 0{\cdot}86 \times 10^{-5}\,cm^2/\text{sec.}$;
Mannite, $0{\cdot}44\,[1 + (25^\circ - 10^\circ)\,0{\cdot}025] = 0{\cdot}60 \times 10^{-5}\,cm^2/\text{sec.}$,

we see that we shall probably not make a very large error, and not take a too high value, if we assume for hydrogen peroxide a diffusion coefficient of $10^{-5}\,cm^2/\text{sec.}$

Summary of the Available Experimental Results.—It will be convenient to preface this discussion by a summary of the available results.

In neutral and acid solutions Bredig found that the reaction proceeded as one of the first order, that is, it was expressed by the equation

$$\frac{1}{t}\log\frac{C_0}{C} = K \qquad (1),$$

in which C_0 is the initial concentration of the hydrogen peroxide, C its concentration after the time t, and K a constant. The same equation holds for hæmase, according to Senter's experiments. In alkaline solution, no general formula was found by Bredig to express the results. The constant K is greatly influenced by the addition of certain substances (poisons); it varies more rapidly than proportionally with the concentration of the catalyser, and increases geometrically with change of temperature, rising to its threefold value every 20°.

On the Relative Size and Available Surface of the Particles in Wholly and Partially Poisoned Solutions.—I do not propose to enter into a discussion of the effect of poisons more deeply than is required for the primary objects of the present paper. It seems that two explanations are compatible with Nernst's views. Firstly, in the case of substances which have a very powerful effect, an inactive film may be formed on the particles by chemical action of the poison, whenever the concentration of the latter in the solution is greater than a certain definite value, and the platinum would thus be completely poisoned as soon as this value was exceeded by the small quantity necessary to form the coating. Such an explanation is, however, manifestly not applicable to weak poisons, such as acids and certain electrolytes, the action of which begins at low concentrations, and is not complete until very large values are attained. In this case it seems that the only explanation compatible with Nernst's hypothesis would have to be sought in the tendency of such substances to cause the coalescence and final precipitation of the particles. The influence of alkalies in accelerating the reaction would lie in their tendency to bring about further disintegration of particles which had already undergone partial coalescence.* In any case, however, as has already been pointed out, we may assume that in solutions which are at all stable no particles occur of a diameter greater than 0·5 μ.

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* *Loc. cit.*, vol. 31, p. 272.

The Experimental Results on Dependence of Reaction Velocity on Concentration of the Catalyser can only be Reconciled with the Idea of a Heterogeneous Reaction by Recognising the Important Part Played by Convection Currents.— It is *a priori* clear with regard to the relative *rôle* of diffusion and convection that the latter must be seriously considered, owing to the fact that solid particles suspended in a liquid are known to be in a state of continual movement performing the so-called Brownian motions. Besides, in the more concentrated solutions oxygen-bubbles are given off, and cannot fail to stir the liquid.

As a matter of fact, a brief examination of the results summarised above suffices to show that they are not in agreement with Nernst's hypothesis, if we suppose diffusion alone, without convection, to be responsible for the neutralisation of changes of concentration. We may even go further, and say that the fact that K increases more rapidly than proportionally with the concentration of the catalyser cannot be reconciled with the idea of a heterogeneous reaction at all, unless the process taking place on the surface of one of the particles influences that of its neighbours by some non-chemical means, such as the production of convection currents. If we were dealing with a stationary liquid, whatever the chemical mechanism of the reaction may be, the amount of substance decomposed in a given time at the beginning of the experiment would be proportional to the number of particles, that is, to the concentration of the platinum. Now, the constant K may be taken as a direct measure for this amount, as is clear from the following relation arising from Equation 1,

$$-\frac{dC}{dt} = CK \qquad (2).$$

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* Bredig, *loc. cit.*, vol. 31, p. 306, note 2.

Bredig's results thus contradict the idea of a heterogeneous reaction taking place in a stationary liquid. They, however, become intelligible if we consider the influence of convection. Proceeding on lines similar to those adopted by Nernst, we may assume each particle to be surrounded by a film of adhering liquid, the thickness of which depends very largely on the amount of motion taking place in the solution. The thinner the film, the greater will be the flow of solute to the particles, and the greater, therefore, the velocity of the reaction. Now, in the solutions containing large quantities of the catalyser, considerably more convection is produced than in those in which small quantities are present, owing to the brisker evolution of bubbles of oxygen gas, and in this fact the explanation of Bredig's result is very probably to be sought.

In accordance herewith, we should expect that in solutions containing very small amounts of catalyser, and in which, consequently, the evolution of oxygen is so slight that no gas-bubbles are produced, no deviation from the law of proportionality between K and the concentration of the catalytic particles would occur.

This point has not been specially tested by Bredig, but by collating results scattered over his paper, we may gather that the conclusion drawn is correct. Thus, in Table 11, first part, p. 291, we have for a concentration of N/30000 platinum an average value of K of approximately 0·016 min.$^{-1}$, whereas, at the end of Table 13, p. 300, we have, at a later date, with the same platinum solution, diluted to a concentration of N/300000 K, approximately equal to 0·0012 min.$^{-1}$, *i.e.*, only slightly less than one-tenth of the former value.

In agreement with this, Senter found that in his very dilute solutions the velocity of the reaction was proportional to the concentration of the catalyser, whereas in more concentrated solution it increased more rapidly.

The Experimental Results on Dependence of Reaction Velocity on Temperature Cannot be Reconciled with Nernst's Hypothesis unless Convection Plays an Important Part.—Bredig's results regarding the influence of temperature cannot be reconciled with Nernst's hypothesis if we suppose the particles and liquid to be stationary. In this case the only effect of a rise of temperature would be to increase the diffusion coefficient of the solute by about 2½ per cent. per degree, and the result of doing this can be seen from the following theorem:—If concentrations in a liquid are determined solely by diffusion according to Fick's law, in such a manner that they arise out of a given initial state and a condition not defined as a time-relation which is maintained uniformly throughout the experiment (such as the one that the concentration is permanently kept at zero on the surface of stationary particles of any shape and distribution whatever), then the concentration at any point may be expressed as a function only of the co-ordinates of that point and the product of the diffusion coefficient and the time, the average concentration being a function only of the product of the diffusion coefficient and the time.*

By the application of this theorem to Equation 1, we find that if this equation were the result solely of diffusion in a stationary liquid, then in order that it may conform with Nernst's hypothesis, the constant K must increase by about $2\frac{1}{2}$ per cent. per degree. This is a far smaller increase than that actually observed. If, however, convection takes place with increasing efficiency as the temperature rises, there is so far no contradiction with Nernst's hypothesis.

If the Distribution of the Particles is Fine Enough, the Concentration Throughout the Liquid will be Practically Uniform.—It should be pointed out here that if only the disintegration of the particles is great enough and their distribution consequently fine enough, changes of concentration occurring on their surfaces will be transmitted practically instantaneously throughout the liquid by diffusion. In this case, if Nernst's hypothesis is correct, the concentration of the whole solution would be instantaneously reduced to zero, but even if this hypothesis does not hold, the idea of a heterogeneous reaction would demand that the velocity of reaction at a given concentration of the solute should be proportional to the concentration of the catalysing particles.

If Nernst's Hypothesis Holds, the Reaction Velocities Found by Bredig must be Greater than those Calculated for a Stationary Liquid.—We have thus seen that convection currents play an important part in the processes under discussion, and always tend to accelerate them. The last-named fact opens up a way by means of which to apply a direct test to Nernst's hypothesis. If, on this hypothesis, an expression could be calculated which is equal to or smaller than the reaction velocity under the smallest conceivable amount of convection, this expression should always be smaller than the experimentally found values, and if it is equal to or greater than the latter, this would prove that Nernst's hypothesis must be discarded in the cases under investigation, *i.e.*, that the concentration of hydrogen peroxide on the surfaces of the particles is not permanently maintained at zero.

As has already been stated, we possess an upper limit for the diameter of the particles, and we shall assume them all to be spheres of this diameter, thus being certain to obtain a minimum value for reaction velocity. It is evident that if a given volume were distributed in pieces of larger surface and more especially in flat pieces or in pieces of smaller diameter, a much larger reaction velocity would arise.

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* There is no difficulty whatever in proving this theorem in a purely mathematical way, but it becomes immediately obvious, when we remember that we can give the diffusion coefficient κ any desired value $a\kappa$ by increasing the unit of time to its a-fold value. In the new units any interval of time which before was expressed by t is now given by t/a, and in order that concentrations after any real interval of time may remain unaltered, the above theorem must hold.

We again assume each particle to be surrounded by an adhering film of liquid, in which no convection occurs, in such a manner that the greater the amount of stirring or motion in the solution, the smaller the thickness of this layer. On the outside of the film the concentration may be considered to have a definite value which is not exceeded in any part of the solution. If the film is exceedingly thin, then the flow of solute to the particle will continually be very great and roughly inversely proportional to the thickness of the film. If the latter, however, be thick, then, as will be seen in the sequel, the flow of solute to the particle rapidly decreases to a value corresponding to a permanent distribution of concentration in such a manner that this flow becomes practically independent of the thickness of the layer and only depends on the concentration outside.

It should be pointed out here that a limit is set to the thickness of the films by the fact that their total volume must be smaller than that of the liquid. If each layer with its enclosed particle forms a sphere of radius R, and N is the number of particles per unit volume, we, therefore, have the inequality

$$\tfrac{4}{3}\pi R^3 N < 1 \qquad (3).$$

The concentration outside the films, as will be seen in the sequel, is practically the average concentration of the liquid. If, therefore, the particles are far apart, we shall by always assuming the permanent flow to take place, corresponding to a very (infinitely) thick layer, on the outside of which the average concentration of the liquid is maintained, obtain values for reaction velocity, which may be taken to be those belonging to the minimum conceivable amount of convection.

Deduction of a Formula for the Reaction Velocity Corresponding to a Minimum Amount of Convection.—We have to deal with the following case:—A sphere of given radius r is immersed in a solution of the concentration C_0. On its surface the concentration is kept continually at zero, and at a distance R from its centre the concentration D is always to be found, which is not exceeded in any part of the liquid. The smallest conceivable amount of solute, Fdt, that could under these conditions flow to the sphere in the time dt, is the value which Fdt would have if the conditions we have assumed had already been in operation for an infinite period of time. This would mean that a permanent state had been established, and as it is our object to find a minimum value for the substance removed, the first part of our problem consists in determining Fdt corresponding to the permanent state.

The total amount of solute $F_{(x)}dt$ flowing in the time dt towards the centre of the sphere across a concentric spherical surface of radius x is given by

$$F_{(x)}dt = 4\pi\kappa x^2 \frac{\partial c}{\partial x}\, dt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4),$$

if κ indicates the diffusion coefficient of the solute, and c its concentration at the points under consideration. From this equation we arrive by considerations of a well-known kind* at the relation

$$\frac{\partial c}{\partial t} = \kappa\left(\frac{\partial^2 c}{\partial x^2} + \frac{2}{x}\frac{\partial c}{\partial x}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5).$$

For the permanent state we have $\partial c/\partial t = 0$, the limiting conditions being

$$c = 0 \quad \text{for} \quad x = r \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6),$$

$$c = \mathrm{D} \quad \text{for} \quad x = \mathrm{R} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7).$$

The result of the integration under these conditions is

$$c = \mathrm{D}\frac{\mathrm{R}}{\mathrm{R}-r}\cdot\frac{x-r}{x} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8),$$

and the amount removed at the surface of the small sphere in the time dt follows from Equation 4

$$\mathrm{F}dt = 4\pi\kappa r\gamma \mathrm{D}dt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9),$$

the quantity γ being defined by

$$\gamma = \frac{\mathrm{R}}{\mathrm{R}-r} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10),$$

and decreasing from infinity to 1 as R increases from r to infinity.

We now have to show that in all the cases we are dealing with the quantity D does not differ appreciably from the average concentration C of the liquid. Indicating again by N the number of particles per unit volume of solution, and by v their total volume, then

$$\tfrac{4}{3}\pi r^3 \mathrm{N} = v \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11),$$

and C, which is equal to the total amount of solute per unit volume of liquid, is given by

$$\mathrm{C} = \mathrm{N}\int_r^{\mathrm{R}} 4\pi x^2 c\,dx + (1 - \mathrm{N}\tfrac{4}{3}\pi\mathrm{R}^3)\,\mathrm{D}.$$

Eliminating c and N from this expression by means of Equations 8 and 11 and simplifying, we obtain

$$\mathrm{C} = \mathrm{D}\left\{1 - \tfrac{1}{2}v\left[\left(\frac{\mathrm{R}}{r}\right)^2 + \frac{\mathrm{R}}{r}\right]\right\}.$$

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* See *e.g.*, Fourier's "Analytical Theory of Heat," §§ 112 and 113.

This equation, taken in conjunction with the inequality 3, and with Equation 11, leads to the conclusion that the greatest conceivable value for the difference between C and D is $\frac{1}{2}D(v^{\frac{1}{3}} + v^{\frac{2}{3}})$.

Now, in all the cases we have to consider v is smaller than 10^{-6}, so that we may, without appreciable error, make D equal to C. Remembering, also, that the decrease $-dC$ of C in the time dt equals $NFdt$, and expressing the radii of the spheres by their diameter L, we obtain from Equations 9 and 11

$$-dC = \frac{12\kappa v}{L^2}\gamma C dt,$$

from which, by utilising the limiting condition $C = C_0$ for $t = 0$, we find by integration

$$\frac{1}{t}\log\frac{C_0}{C} = K \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12),$$

the constant K being given by the equation

$$K = \frac{12\kappa v}{L^2}\gamma \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (13),$$

and having the minimum value

$$K = \frac{12\kappa v}{L^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (14).$$

Examples to Show that Equations 9, 12, *and* 14, *are a Close Approximation to the Correct Result.*

(a) *A Sphere in Infinite Space.*—In deducing the foregoing equations, we assumed the permanent state to be always produced instantaneously, and we have made it clear that the result thus obtained for the rate of change of concentration will certainly not be too large. In reality, when the spheres are so small as those we have to deal with, and the volume they draw solute from more than a millionfold as great as their own, no appreciable error is made by our assumption. We can readily prove this by integrating Equation 5 completely for simple cases, and showing that the results approximate very quickly to those we have calculated.

As a first example, we determine the amount of solute which would be removed by each sphere after the time t if it were placed in an infinite amount of solution at the beginning of the experiment. For this purpose we calculate an expression for the concentration throughout the liquid at any time t by integrating Equation 5 under the limiting condition $c = D$ between $x = r$ and $x = \infty$ for $t = 0$, and the condition expressed by Equation 6.

The integral obtained is

$$c = \mathrm{D} - \frac{\mathrm{D}r}{x} + \frac{2\mathrm{D}r}{\sqrt{\pi}x}\int_0^{\frac{x-r}{2\sqrt{\kappa t}}} dq e^{-q^2},$$

a result which can be verified without difficulty.

The amount of solute S removed by the sphere after the first t seconds is

$$\mathrm{S} = 4\pi\kappa r^2 \int_0^t \frac{\partial c}{\partial x}\, dt \text{ when } x = r$$

$$= 4\pi\kappa \mathrm{D} r t + 8\sqrt{\pi\kappa t}\, r^2 \mathrm{D}$$

The first member on the right side of this equation is identical with the value which follows for R equal infinity from the Equation 9 we previously employed. Making $2r = 5 \times 10^{-5}$ cm, $\mathrm{K} = 10^{-5}$ cm²/sec., we can calculate that the difference between this quantity and S amounts to only 0·9 per cent. of S after 1 second.

(b) *A Sphere in a Large Enclosed Spherical Space.*—The close approximation of the result expressed by Equations 12 and 14 to the correct value for stationary liquids, in which the radius of action of each spherical particle is great compared with its own diameter, is specially made clear by the full calculation of the case in which one of the spherical particles is placed in the centre of a spherical vessel of large diameter filled with solute. In this case we have to integrate Equation 5, the limiting conditions being firstly that no solute can pass through the wall of the vessel. Indicating the radius of the latter by R, this means that

$$\mathrm{F_R} = 0, \textit{ i.e.}, \text{ according to Equation 4, that } \frac{\partial c}{\partial x} = 0, \text{ for } x = \mathrm{R}.$$

We have besides the limiting condition expressed by Equation 6 and the condition

$$c = \mathrm{C}_0 \quad \text{between } x = r \quad \text{and } x = \mathrm{R}, \quad \text{for } t = 0.$$

The differential equation can be integrated subject to these limits by methods similar to those employed in §§ 283 to 293 of Fourier's Analytical Theory of Heat for the determination of changes of temperature in a solid sphere. The following result is thus obtained:—

$$c = \frac{1}{x}\left[a_1 e^{-\kappa n_1^2 t} \sin n_1 (x - r) + a_2 e^{-\kappa n_2^2 t} \sin n_2 (x - r) + \ldots\right],$$

the numbers n being determined as the successive roots of the equation

$$\frac{\tan n(\mathrm{R} - r)}{n\mathrm{R}} = 1,$$

and the coefficients a by the equation

$$a_p = C_0 \frac{\int_r^R x \sin n_p (x-r)\, dx}{\int_r^R \sin^2 n_p (x-r)\, dx} = C_0 \frac{1}{n_p} \frac{\frac{1}{n_p} \sin n_p (R-r) - R \cos n_p (R-r) + r}{\frac{1}{2}(R-r) - \frac{1}{4n_p} \sin 2n_p (R-r)}.$$

This system of equations is simplified, and the dimensions of the quantities occurring in them made clear by introducing in place of a and n the quantities α and ν defined by the relations:

$$n(R-r) = \nu \quad \text{and} \quad a_p/n_p = \alpha_p C_0 (R-r)^2.$$

These quantities α and ν are functions only of the non-dimensional number ϵ defined by the equation

$$\epsilon = \frac{r}{R-r}.$$

After several transformations the final system of equations is arrived at.

$$C = \frac{C_0(R-r)}{x}\left[\alpha_1 \nu_1 e^{-\kappa t \frac{\nu_1^2}{(R-r)^2}} \sin \nu_1 \frac{x-r}{R-r} + \alpha_2 \nu_2 e^{-\kappa t \frac{\nu_2^2}{(R-r)^2}} \sin \nu_2 \frac{x-r}{R-r} + \ldots\right] \ldots\ldots\ldots \quad (15),$$

the quantities ν being found as the successive roots of the equation

$$\frac{\tan \nu}{\nu} = 1 + \epsilon \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (16),$$

and the quantities α by the equation

$$\alpha_p = \frac{2\epsilon}{\nu_p^2 [1 - (1+\epsilon)\cos^2 \nu_p]} \ldots\ldots\ldots\ldots\ldots\ldots \quad (17).$$

Values of time always exist for which the infinite series can practically be replaced by its first member. If ϵ be small the values for ν_1^2 and α_1 arising out of Equations 16 and 17 may be taken as

$$\nu_1^2 = 3\epsilon, \qquad \alpha_1 = \frac{1}{3\epsilon},$$

and the whole expression simplified to

$$c = C_0 \frac{x-r}{x} e^{-12\kappa t \epsilon^2 / L^2}.$$

The concentration varies with distance from the small sphere in the identical manner we found previously in Equation 8, and we have already proved that this being so the average concentration C may without appreciable error be assumed to be equal to the upper conceivable limit of c. We thus have

$$C = C_0 e^{-12\kappa t \epsilon^2 / L^2},$$

an equation which by a slight transformation becomes identical with Equations 12 and 14.

The Application of Equation 14 to Bredig's Results Shows that they contradict Nernst's Hypothesis.—Equation No. 12 is identical in form with No. 1 which Bredig found to represent his experimental results. As the constant K is a measure for reaction velocities under corresponding conditions (see Equation 2), we can submit Nernst's hypothesis to the test we have outlined above by a comparison of the theoretical minimum value for K of Equation 14 with the experimental values found by Bredig.

We employ the results given by him in Table 7 'Zeitschrift f. Physikalische Chemie,' vol. 31, p. 285. The concentration of the platinum was here 31500^{-1} g-atom of platinum per litre, which is approximately 3150000^{-1} c.c. of platinum per c.c. We thus have to substitute $\kappa = 10^{-5}\text{cm}^2/\text{sec}$, $L = 5 \times 10^{-5}\text{cm}$, and $v = 3150000^{-1}$ into Equation 14, and find

$$K = \frac{12 \times 10^{-5}}{(5 \times 10^{-5})^2 \times 3150000} = 0{\cdot}0152 \text{ sec.}^{-1} = 0{\cdot}91 \textit{ min.}^{-1}.$$

Whereas the average value of Bredig's experiments in which $\frac{N}{2000}$ Na_2HPO_4 was present amounted to only $\frac{0{\cdot}016}{0{\cdot}4343} = 0{\cdot}037$ min.$^{-1}$, that is about one twenty-fifth of the calculated minimum number, and the average value in a solution containing no electrolyte whatever was $\frac{0{\cdot}024}{0{\cdot}4343} = 0{\cdot}055$ min.$^{-1}$, that is about one-sixteenth of the calculated value.

Even in alkaline solution in which the reaction proceeds very much faster, the velocity is smaller than the calculated value, whereas on Nernst's hypothesis it ought, as already explained, to be much greater. We employ the numbers given by Bredig in Table 12, p. 297, for a $\frac{N}{32}$ NaOH solution, which probably correspond to the very greatest velocity measured by him. Here we have $v = 300000^{-1}$ g-atom of platinum per litre, that is approximately $v = 30000000^{-1}$ c.c. per c.c., the other quantities being the same as above. By Equation 14 we thus calculate

$$K = 0{\cdot}0016 \text{ sec.}^{-1} = 0{\cdot}096 \text{ min.}^{-1},$$

whereas the average value of the constant given by Bredig amounts to $\frac{0{\cdot}0205}{0{\cdot}4343} = 0{\cdot}0472$ min.$^{-1}$, that is about half of the calculated minimum value. We thus see that Bredig's reactions proceed far too slowly to allow us to reconcile them with Nernst's hypothesis.

An Equation of the Form of No. 1 expresses the Result if the Velocity of the Reaction Occurring on the Surface of the Particles is Proportional to the Concentration of the Solution in Immediate Contact with them.—The fact that the law obeyed by Bredig's reactions differs only in the magnitude of a constant from the formula we have deduced on Nernst's hypothesis might, perhaps, seem an argument in favour of the latter.

We now proceed to show that we can obtain an equation of the same form as Nos. 1 and 12, but differing from Nos. 13 and 14 in the value of the constant K, if we drop altogether the assumption that equilibrium is permanently maintained on the boundary between the particles and the solution, *i.e.*, that the concentration of the hydrogen-peroxide is permanently maintained at zero. Instead we assume that the amount F*dt* acted upon in the time *dt* by each particle is proportional to the concentration C′ of the solute actually in contact with it. Retaining the same notation we employed above, we thus have

$$\mathrm{F}dt = \alpha 4\pi r^2 \mathrm{C}' dt \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (18),$$

α being a constant. The amount of substance removed on the surface of the particle must be replaced by diffusion from the interior of the solution as a discontinuity of concentration would otherwise occur. It can be expressed in terms of κ, γ and $\mathrm{D} - \mathrm{C}'$ by making use of Equation 9. This Equation was deduced on the assumption that the concentration on the surface of the particles is zero. As absolute values of concentration do not occur in Fick's law of diffusion, it is evident that we may generalise the result so as to comprise the case that the concentration on the surface of the particles is C′ by replacing D of Equation 9 by the difference $\mathrm{D} - \mathrm{C}'$. We thus obtain

$$\mathrm{F}dt = 4\pi\kappa r\gamma (\mathrm{D} - \mathrm{C}') dt \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (19)$$

Eliminating C′ from Equations 18 and 19, we find

$$\mathrm{F}dt = \frac{4\pi\alpha\kappa r^2\gamma \mathrm{D}}{\alpha r + \kappa\gamma} dt,$$

from which we deduce a formula identical with No. 12, by reasoning exactly analogous to that employed to establish it. The constant K in the present case, however, has the value

$$\mathrm{K} = \frac{12\alpha\kappa\gamma v}{\mathrm{L}(\alpha \mathrm{L} + 2\kappa\gamma)},$$

the number γ varying according to the amount of convection from 1 to infinity, as is clear from Equation 10, and the number α having any positive value, which may be called the velocity constant proper of the reaction.

Thermodynamical Criticism of Nernst's Hypothesis.—In conclusion, it may be useful to criticise the principle put forward by Nernst from a thermodynamical point of view. The essence of it is contained in the following two sentences:—"Many facts lead to the assumption that equilibrium is established on the boundary of two phases, with extremely great velocity. Such a behaviour is also, it seems, theoretically necessary, for, otherwise, finite differences of chemical potential would occur on the boundary of two phases, *i.e.*, at infinitely near points, which would manifestly lead to infinitely great forces and reaction velocities."

As is well known, we owe Nernst the calculation of the diffusion coefficient of an electrolyte, which probably forms the most brilliant instance we possess for the deduction of the velocity of a natural process from thermodynamical data. In this case, the force is calculated which may be considered to act upon a g-ion of electrolyte (force due to osmotic pressure) in a solution of uneven concentration, and by assuming the mobility of the ions to be the same, whether under the influence of forces due to difference of concentration, or under that of electric forces, the diffusion coefficient of the electrolyte can be calculated. Here we have an instance to which the considerations quoted above from Nernst apply beyond doubt. We may put the matter in the following form :—If a discontinuity of concentration were to occur in a solution, we should have finite differences of thermodynamical potential at infinitely near points, or, in other words, finite amounts of work would become available in order to move a given quantity of solute an infinitely small, or, at least, a very small way. Now, as the work required to overcome internal resistance in moving a finite quantity of solute through an infinitely small stretch of solution is infinitely small, a condition such as the one considered would lead to an infinite flow of solute. Similarly, if a solid be brought together with its unsaturated solution, finite amounts of free energy are available to dissolve a given quantity. Now, in this case, although it is not *a priori* certain, yet it is exceedingly probable that the work is practically infinitely small which is necessary to overcome internal resistance in transferring substance an infinitely small distance from the solid to the liquid phase. We may, therefore, conclude that a practically infinite instantaneous flow would occur, and bring about equilibrium on the boundary. Similar considerations probably apply to most physical processes, or, at any rate, to such as are capable under any conditions of occurring in a reversible manner.

When, however, we turn to chemical processes, we meet with a difference in principle. If we wish to consider a chemical reaction as a transference of atoms over molecular distances, we can no longer say that the work in overcoming internal friction during this transference is a negligible quantity for a finite amount of substance. If it were, it is evident that all chemical reactions in homogeneous systems during which finite amounts of free energy are destroyed; should be instantaneous. This is, however, not the case. In fact, it is not clear why a chemical reaction should proceed with greater velocity on the boundary of two phases than in the interior of one of them. It is not to be denied that many chemical reactions do take place instantaneously on the boundary of two phases, and a considerable number of interesting cases have been investigated by Brunner,* which evidently conform to this rule. It does not, however, seem probable that a useful purpose would be served in considering this rule to hold universally.

I have examined consequences drawn from it with regard to irreversible electrolytic reductions, and do not find them to agree with facts.† Many other cases might also be brought forward that would be very difficult to reconcile with this theory, *e.g.*, the great difference of velocity shown by metals in dissolving in different acids,‡ catalysis by substances such as nitrogen peroxide during the solution of copper in nitric acid, and others.

In conclusion, the author desires to say that he has had the advantage of discussing the matter treated in this paper with Dr. Senter and Professor Poynting, for which he acknowledges his indebtedness.

"On Galvanic Cells produced by the Action of Light. Preliminary Communication."§

By M. WILDERMAN, Ph.D., B.Sc. (Oxon). Communicated by Dr. LUDWIG MOND, F.R.S.

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(From the Davy-Faraday Laboratory of the Royal Institution.)

In my paper "On Chemical Statics and Dynamics" ('Phil. Trans.,' A, vol. 199, 1902, p. 337), and especially 'Zeit. Physik. Chemie,' vol. 42, 1902, pp. 316—335, I deduced, from thermodynamics, the laws experimentally found by me for velocity of chemical reaction, and for chemical equilibrium under the action of light, from the fundamental conception that the chemical potential of substance in light and in the dark is different, becoming greater in light. The foundation for this conception was that two metallic plates immersed in a liquid and connected to a circuit form a "galvanic" combination, when one plate is exposed to light while the other is kept in the dark; and, according to Gibbs' equation, $v'' - v' = a_a(\mu_a' - \mu_a'')$, no galvanic cell could be formed, unless the chemical potentials at the two electrodes were different in light and in the dark.

The experiments of Becquerel and Minchin left students to infer that the E.M.F. observed is due to "surface phenomena," because, with AgCl, AgBr, AgI plates both observed currents sometimes in one direction, sometimes in the other, and in every experiment different curves and mysterious phenomena ("very curious cases of inversion of the current") were observed. No galvanic combination we know of gives a current in one direction at one time, in the opposite at another, the anode and cathode exchanging their parts.

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* 'Ztschft. Phys. Chem.,' vol. 47, p. 56 (1904).

† Faraday Society, October 25, 1904.

‡ Ostwald, 'Grundlinien d. anorganischen Chemie,' p. 249.

§ This paper contains a preliminary account of the author's further researches on "Chemical Statics and Dynamics of Reversible and Irreversible Systems under the Action of Light."

Not only were the deflections of the galvanometer observed, but all the curves in all their complexity were studied and photographed from beginning to end, including the induction and deduction periods. I succeeded, after much trouble, in making the investigation quantitative instead of qualitative, as hitherto; the results observed were studied, and considered in connection with the chemical composition of the heterogeneous system, and with those chemical reactions, previously unknown to us, which take place in the different systems under the action of light; the complex nature of the phenomena observed was found, quantitatively separated into constituents, and freed from interfering concomitants, etc.

Though the ampères and volts measured were mostly exceedingly small (the first had to be measured in units of 10^{-9}, and the second in units of 10^{-6}), the photographed curves obtained show that the experimental difficulties in this region were quite overcome, since concordant results were obtained on repetition of the experiments.

As the result of more than 3 years' work, I find that there is, under the action of light, a region of galvanic cells as wide and as varied as in the case of ordinary galvanic cells. We have here constant and inconstant cells, reversible and irreversible cells. The chemical reactions and chemical equilibrium in these galvanic combinations are now perfectly clear, yet they are all *sui generis*, all the phenomena being intermixed, and characterised by phenomena of induction and deduction peculiar to light cells only. I succeeded also in placing this region of phenomena on a physico-mathematical basis, testing and proving the equations experimentally in all details. The principal results obtained are:—

(1) The total E.M.F. produced by light consists of an E.M.F. produced by light at a constant temperature, owing to increase of chemical potential, and of solution pressure of the exposed plate, and of a thermo-E.M.F. caused by one of the two plates in contact with the liquid being heated by light. Both E.M.F.'s are found to be directly proportional to the intensity of light, and both give currents in the same direction, proving that light acts on chemical potential, as well as on solution pressure of the electrode, in the same way as does heat. My generalisation for light: "Each kind of equilibrium between two states of matter (system) is, at constant volume, on exposure to light, shifted in the direction accompanied by greater absorption of light"

(analogous to van't Hoff's "principle of moveable equilibrium" for heat) is thus proved.*

(2) *The phenomena of reversal of the current, etc., observed by* Becquerel and Minchin, are due, not to surface phenomena or different "thicknesses of sensitive layer," but to the fact that their combinations all give inconstant cells showing polarisation, a phenomenon which they and other observers entirely overlooked, since they made no study of the induction and deduction periods. Whenever a consideration of the composition of the heterogeneous system, and of the reactions going on in the same under the action of the current, shows that an inconstant cell should be formed, the curve illustrated by fig. 2 is obtained, the peculiar course of the induction and deduction periods being caused by the principal E.M.F. and the E.M.F. of polarisation being set up simultaneously under the action of light, with different velocities, and diminishing on removal of the light, with different velocities, vanishing almost simultaneously. Whenever a consideration of the composition of the heterogeneous systems, and of the reactions going on in the same under the action of the current, shows that the cell should be reversibly constant, then, provided the action of light upon the plate is such as to allow of the formation of a constant cell, and, provided the plates are so prepared as to avoid the formation of "gas batteries" (for this the E.M.F. in the dark must be made very small—a few millionths of a volt) we get constant cells, the induction and deduction period having a normal course, as illustrated in fig. 1.

(3) The law *governing the induction period in constant* reversible cells is evidently

$$\frac{d\pi}{d\tau} = c\,(\pi_0{}' - \pi)\,(\pi - \pi_0 + \mathrm{K}),$$

i.e., the speed with which the system approaches, on exposure to light, its new state of equilibrium in light (given by the line *d*—*e*, and characterised by the value of constant E.M.F., $\pi_0{}'$) is directly proportional to the remoteness of the system at the given time, τ, from the point of equilibrium in light (given by the value $\pi_0{}' - \pi$, if π is the E.M.F. at the time τ, while $\pi_0{}'$ is the maximum E.M.F. in light), and to the amount of variation already produced by light in the system up to the time τ (given by $\pi - \pi_0$, if π_0 is the initial E.M.F. of the system in the dark) plus a constant K, which is also of the character of an instability constant, *i.e.*, the more the system is removed from its point of equilibrium in light, the quicker it approaches it, and the more the molecules and atoms have been shaken up by light (exposed to light previously to the time τ), the quicker the system approaches the point of equilibrium in light. This gives also the fundamental law of photography, the connection between the amount of silver salts decomposed and the time of exposure, since the E.M.F. is, during this

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* See 'Zeitsch. physik. Chemie,' 1902, p. 332; 'Phil. Mag.,' 1903, vol. 5, p. 223.

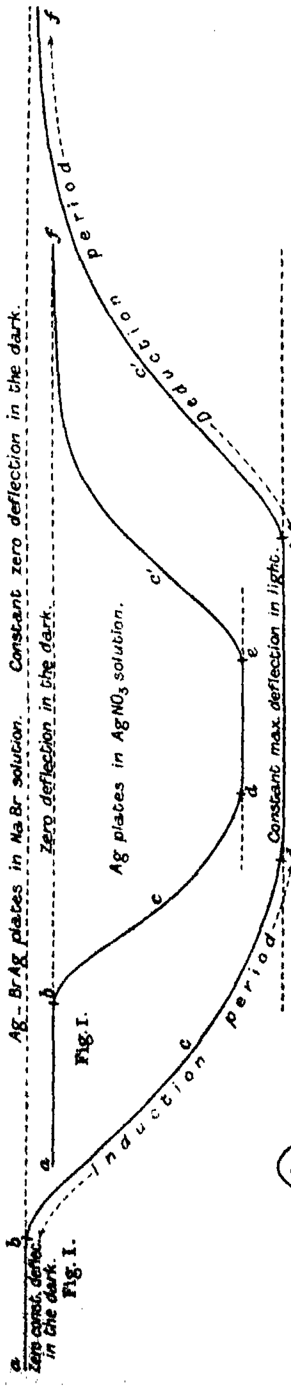

Fig. I.

Fig. I.

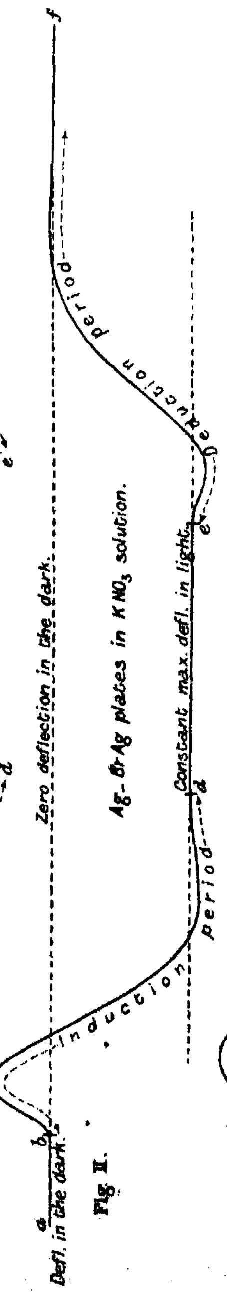

Fig. II.

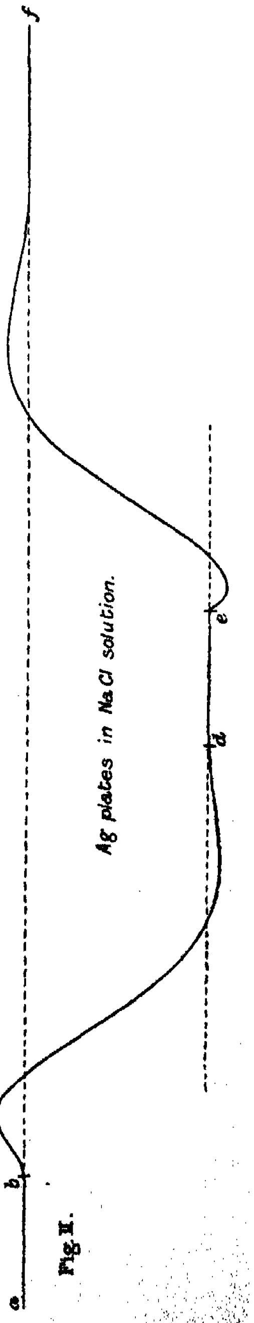

Fig. II.

period, directly proportional to the current, and gives the true measure of the amount of silver salts decomposed by light. The equation for the deduction period is also

$$-\frac{d\pi}{d\tau} = -c'(\pi_0 - \pi)(\pi - \pi_0' + K'),$$

i.e., is directly proportional to the remoteness of the system from the point of equilibrium in the dark, $\pi_0 - \pi$, and to $\pi - \pi_0'$, which gives the amount of variation produced by the removal of the light in the system already, up to the time τ plus a constant K′.

(4) The physico-mathematical theory of "constant cells reversible in respect of the cation" (*e.g.*, Ag plate in light, $AgNO_3$ solution in light, $AgNO_3$ solution in dark, Ag plate in dark) is the following. The result of the process under the action of light consists :—

(1) In one gramme-atom of the cation ($\overset{+}{Ag}$) of a higher chemical potential passing from the electrode (Ag) in light into the solution of the salt of the electrode in light.

(2) From the solution in light the gramme-atom of the cation passes to the solution in dark, transforming there into cations of a lower chemical potential, passing a deduction period.

(3) Finally from the solution in dark the gramme-atom of the lower chemical potential separates upon the electrode (Ag) in dark.

Let the solution pressure of the plate be in dark P_d, the osmotic pressure of the cations (+Ag) in the solution in dark p_d. Then, since the chemical potential of a substance is different (greater) in light than in dark, the solution pressure of the same plate in light will be P_l, and the osmotic pressure of the cations of the same concentration in light will be p_l. If now we calculate the work done by such a system, when, under the action of light, 1 gramme-atom of Ag passes from the plate in light to the plate in dark, we get

for (1) $\quad E_1 = 0{\cdot}860T \log_e \frac{P_l}{p_l} . 10^{-4}$ volt;

for (2) $\quad E_2 = 0{\cdot}860T \frac{u-v}{u+v} \log_e \frac{p_l}{p_d} . 10^{-4}$ volt (very nearly);

for (3) $\quad E_3 = 0{\cdot}860T \log_e \frac{P_d}{p_d} . 10^{-4}$ volt;

and

$$\Sigma E = E_1 + E_2 - E_3 = 0{\cdot}860T \left(\log_e \frac{P_l}{P_d} - \frac{2v}{u+v} \log_e \frac{p_l}{p_d}\right) 10^{-4} \text{ volt} .. \quad (I)$$

gives the value of the E.M.F. of such combinations under the action of light. This equation shows :—

(1) The E.M.F. of such a combination must be independent of concentration, *i.e.*, $\Sigma E - \Sigma E' = 0$.

This was found experimentally to be the case.

(2) Experiments were made which showed that both the value

$$0{\cdot}860\,\mathrm{T}\,\frac{2v}{u+v}\,\log_e\frac{p_l}{p_d}\,.\,10^{-4}\ \text{volt}$$

and the electrical potential difference between the illuminated and the non-illuminated solution can be neglected, in comparison with the electrical potentials of the plates and solution. Thus Equation (I) can be written

$$\Sigma\mathrm{E} = 0{\cdot}860\,\mathrm{T}\left(\log_e\frac{\mathrm{P}_l}{\mathrm{P}_d}\right)10^{-4}\ \text{volt}\ \ldots\ldots\ldots\ldots\ldots\ \ \text{(IV)}.$$

(3) Since P_l is $>\mathrm{P}_d$, $\Sigma\mathrm{E}$ is positive, *i.e.*, the current must flow from the plate in light to the plate in dark, as was actually found.

(4) From $\Sigma\mathrm{E} = 0{\cdot}860\,\mathrm{T}\log_e\frac{\mathrm{P}_l}{\mathrm{P}_d}\,.\,10^{-4}$ volt or $\epsilon_0\Sigma\mathrm{E} = \mathrm{RT}\log_e\frac{\mathrm{P}_l}{\mathrm{P}_d}$, we get on differentiating and putting $\frac{d\mathrm{P}_d}{d\mathrm{T}} = \frac{-\rho+\mathrm{RT}}{\mathrm{T}v}$, $\frac{d\mathrm{P}_l}{d\mathrm{T}} = \frac{-\rho'+\mathrm{RT}}{\mathrm{T}v}$ (where ρ and ρ' are the heat of transformation of Ag into $\overset{+}{\text{Ag}}$ ions in light and in dark), a law, analogous to that of Gibbs and Helmholtz for ordinary galvanic cells :

$$\epsilon_0\Sigma\mathrm{E} = \rho'' + \frac{\epsilon_0 d\Sigma\mathrm{E}}{d\mathrm{T}}\,.\,\mathrm{T}\ \ldots\ldots\ldots\ldots\ldots\ldots\ \ \text{(VI)}.$$

(5) Equation (VI) allows us to calculate the heat of reaction (ρ'') from the E.M.F.s observed; ρ and ρ', or the heat of transformation of Ag into $\overset{+}{\text{Ag}}$ cations must evidently be different in light and in dark.

(6) By Equation (IV) we can calculate both the ratio of the two solution pressures of the same electrode in light and in dark, from the E.M.F. observed, and also the absolute value of P_l if P_d is known otherwise.

(7) It was found experimentally that the E.M.F. created by light, or the work done by the system under the action of light, is directly proportional to the intensity of light.*

(5) The physico-mathematical theory of "constant cells reversible in respect of the anion" (*e.g.*, Ag-BrAg plate in light, KBr solution in light, KBr solution in dark, Ag-BrAg plate in dark) is the following.

The result of the process under the action of light consists of :—

(1) One gramme-atom of the anion ($\overset{-}{\text{Br}}$) of a higher chemical potential passes from the electrode Ag-BrAg in light into the solution containing a salt of the same acid (BrK) as the salt (BrAg) covering the metal plate Ag.

(2) The gramme-atom of the $\overset{-}{\text{Br}}$ ions passes from the solution in light to the solution in dark, transforming into anions of a lower chemical potential; and

(3) The gramme-atom of the $\overset{-}{\text{Br}}$ ions in the dark of the lower chemical potential separates from the solution upon the electrode in the dark.

If we now calculate the maximum work done by such a system, when under the action of the current 1 gramme of anion ($\overset{-}{\text{Br}}$) passes from the plate in light to the plate in dark, putting P_l, P_d, for the solution pressures of the electrodes in respect of the anion in light and in dark and p_l and p_d for the osmotic pressures of the anions in light and in dark, we get

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* See 'Zeitsch. physik. Chemie,' 1902, pp. 319 and 333; 'Phil. Mag.,' 1903, vol. 5, pp. 211, 224.

for (1) $$E_1 = 0{\cdot}860T \log_e \frac{p_l}{P_l} . 10^{-4} \text{ volt};$$

for (2) $$E_2 = 0{\cdot}860T \frac{u-v}{u+v} \log_e \frac{p_l}{p_d} . 10^{-4} \text{ volt (approximately)};$$

for (3) $$E_3 = 0{\cdot}860T \log_e \frac{p_d}{P_d} . 10^{-4} \text{ volt};$$

and

$$\Sigma E = E_1 + E_2 - E_3 = 0{\cdot}860T \left(-\log_e \frac{P_l}{P_d} + \frac{2u}{u+v} \log_e \frac{p_l}{P_d} \right) 10^{-4} \text{ volt}, \quad \text{(I)}.$$

This is the general equation. It follows :—

(1) The E.M.F. must be independent of concentration; and this was actually found by direct experiment.

(2) An experimental investigation of the value $0{\cdot}860\,T \frac{2u}{u+v} \log_e \frac{p_l}{p_d}\, 10^{-4}$ volt and of the electrical potential difference between the illuminated and not illuminated solution showed in two different ways that it can be neglected, so that we can put

$$\Sigma E = 0{\cdot}860\,T . \log_e \frac{P_d}{P_l} . 10^{-4} \text{ volt} \ldots\ldots\ldots\ldots \quad \text{(IV)}.$$

(3) Equation (IV) shows that, since $P_l > P_d$, the current must flow from the plate in the dark to the plate in the light, as was found experimentally.

(4) The connection is deduced, from Equation (IV), between the E.M.F. of a constant galvanic combination reversible in respect of the anion under the action of light and the heat of chemical reaction in the same, or the chemical energy created by light:

We have

$$\Sigma E = 0{\cdot}860 \left(\log_e \frac{P_d}{P_l} + \frac{2u}{u+v} \log_e \frac{p_l}{p_d} \right) 10^{-4} \text{ volt} = 0{\cdot}860\,T \log_e \frac{P_d}{P_l} . 10^{-4} \text{ volt},$$

or $$n_e \epsilon_0 \Sigma E = RT \log_e \frac{P_d}{P_l}, \text{ and for } n_e = 1,\ \epsilon_0 \Sigma E = RT \log_e \frac{P_d}{P_l}.$$

From this equation we get

$$n_e \epsilon_0 \Sigma E = RTd \left(\log_e \frac{P_d}{P_l} \right) + R \log_e \frac{P_d}{P_l} \frac{dT}{T} = RTd \left(\log_e \frac{P_d}{P_l} \right) + n_e \epsilon_0 \Sigma E \frac{dT}{T} .$$

Now the solution pressures must follow in light and in dark a law similar to Clausius' law of evaporation, and $\frac{d}{dT} \left(\log_e \frac{P_d}{P_l} \right) = \frac{\rho''}{RT^2}$; therefore

$$RTd \left(\log_e \frac{P_d}{P_l} \right) = \rho'' \frac{dT}{T}, \quad \text{and} \quad n_e \epsilon_0 \Sigma E = \rho'' + \frac{n_e \epsilon_0 d\Sigma E}{dT} . T \ldots \quad \text{(VI)},$$

i.e., we get for constant galvanic cells reversible in respect of the anion in light, a law analogous to that of Gibbs and Helmholts and according as $\frac{n_e \epsilon_0 d\Sigma E}{dT}$ is $>$, $=$ or $< \rho''$, the system will take up or not, or give up heat to the surrounding medium.

(5) Equation (VI) allows us to calculate the heat of reaction in galvanic combinations created by light, from the observed E.M.F. and its temperature coefficient. The much greater deflections obtained here induced the author to make vigorous *efforts to determine the temperature coefficient of the E.M.F. observed*, but the enormous experimental difficulties entailed prevented him from getting more than the general result that it can only be very small (experiments with KBr solutions and LiBr solutions). For the same reason the heat of reaction can be determined only approximately.

(6) As to the solution tension in light and in dark, there are differences between cells created by light and ordinary galvanic cells; the first are dependent upon the capacity of absorption of light, the effect of previous illumination, physical changes in the dark, the intensity of light, etc.; all this makes the solution tension of an electrode in light *sui generis*, distinct from the solution tension of ordinary galvanic cells.

(7) The E.M.F. of constant cells reversible in respect of the anion is found also to be directly proportional to its intensity ($\Sigma E = c \,.\, I$ (VII)). Since the light energy falling upon the plate is also directly proportional to the intensity of light, *i.e.*, $L = K \,.\, I$, we have $\Sigma E = \frac{c}{K} L$, *i.e.*, the E.M.F. or the work done by the given system forms always the same fraction of the total light falling upon it, and this must hold good for monochromatic light as well. Since the solution pressure of a substance in the dark is a constant, it follows from (VII) that

$$-\log_e P_l = c \,.\, I : 0{\cdot}860\,T \,.\, 10^{-4} - \log_e P_d \quad \text{and} \quad \log_e P_l = K'' \,.\, I + K''' \qquad \text{(VIII)}$$

This equation gives the variation of the solution pressure P_l of the electrode in light in dependence upon its intensity; if P_d is known from other sources the absolute value of P_l can be calculated for each intensity of light from (VIII).

(6) The theory of thermogalvanic cells is the following. An analysis of the chemical reactions going on in such systems (two equal plates immersed in a solution, one plate being kept at a higher temperature than the other) shows that, *e.g.*, Ag plates in $AgNO_3$ solution must form a constant cell reversible in respect of the cation, that Ag-BrAg plates in NaBr solution must form constant cells reversible in respect of the anion, and Ag plates in NaCl solution must give an inconstant irreversible combination, etc.

The E.M.F. of a thermogalvanic combination evidently consists of: (1) The potential difference between one of the plates and the solution at $T_{,}$, (2) the potential difference of the same plate and the same solution at $T_{,,}$ and (3) the potential difference between two solutions of the different temperatures, *i.e.*, $\Sigma E = E_1 - E_2 + E_3$.

Now we have for the single electrical potential differences $E_1 = \rho + \frac{dE}{dT} T_{,}$ at $T_{,}$, $E_2 = \rho + \frac{dE}{dT} T_{,,}$ at $T_{,,}$ where ρ is the heat of ionisation of one gramme-atom of ions ($\overset{+}{Ag}$ in the above mentioned constant cell reversible in respect of the cation), while E_3 can be put $= E' (T_{,} - T_{,,})$, *i.e.*, the force driving the ions from one part of the solution at one temperature to the other part of the solution at another temperature must be directly proportional to the difference of the two temperatures, because the osmotic pressures are $p_1 = \frac{RT_{,}}{v}$, $p_2 = \frac{RT_{,,}}{v}$ and $p_1 - p_2 = \frac{R}{v}(T_{,} - T_{,,})$. Therefore

$$\Sigma E = \left(\frac{dE}{dT} + E'\right)(T_{,} - T_{,,}) \quad \dots\dots\dots\dots\dots\dots \quad \text{(I)},$$

i.e., the E.M.F. of thermogalvanic cells must be directly proportional to the difference of temperature of the two electrodes, a law which is analogous to the thermo-E.M.F. produced when two metals are in contact, instead of a metal and solution. (The assumption, however, is made that ρ or heat of ionisation can be taken between $T_{,}$ and $T_{,,}$ to remain constant.)

The laws for thermogalvanic cells can be deduced in another way from the solution pressures of the electrodes and the osmotic pressures of the solution. We take the system (Ag, NO_3Ag sol.)$T_{,}$ (NO_3Ag sol., Ag)$T_{,,}$.

We have

$$E_1 = 0{\cdot}860 T_1 \log_e \frac{P_{T_{,}}}{p_{T_{,}}} . 10^{-4} \text{ volt}; \quad E_2 \doteq 0{\cdot}860 T_{,,} \log_e \frac{P_{T_{,,}}}{p_{T_{,,}}} . 10^{-4} \text{ volt};$$
$$E_3 = E'(T_{,} - T_{,,});$$

and

$$\begin{aligned}\Sigma E &= E_1 - E_2 + E_3 \\ &= 0{\cdot}860\left(T_{,} \log_e \frac{P_{T_{,}}}{p_{T_{,}}} - T_{,,} \log_e \frac{P_{T_{,,}}}{p_{T_{,,}}}\right) 10^{-4} \text{ volt} + E'(T_{,} - T_{,,}) \\ &\qquad \dots\dots\dots\dots \quad \text{(I)},\end{aligned}$$

where $P_{T_{,}}$, $P_{T_{,,}}$ are the solution pressures of the silver electrodes at $T_{,}$ and $T_{,,}$. Similarly we get for cells reversible in respect of the anion

$$\Sigma E = 0{\cdot}860\left(T_{,} \log_e \frac{p_{T_{,}}}{P_{T_{,,}}} - T_{,,} \log_e \frac{p_{T_{,,}}}{P_{T_{,,}}}\right) 10^{-4} \text{ volt} + E_1'(T_{,} - T_{,,}) \dots \text{(II)}.$$

Since $p_{T_{,}}$, $p_{T_{,,}}$ are directly proportional to the absolute temperature, we have for systems reversible in respect of the cation

$$p_{T_{,}} = a\mu T_{,}, \qquad p_{T_{,,}} = a\mu T_{,,},$$

and

$$\begin{aligned}\Sigma E = {} & 0{\cdot}860 (T_{,} \log_e P_{T_{,}} - T_{,,} \log_e P_{T_{,,}}) 10^{-4} \text{ volt} \\ & + 0{\cdot}860 (T_{,,} \log_e a\mu T_{,,} - T_{,} \log_e a\mu T_{,}) 10^{-4} \text{ volt} + E'(T_{,} - T_{,,}) \dots \quad \text{(I')},\end{aligned}$$

and for systems reversible in respect of the anion,

$$\begin{aligned}\Sigma E = {} & 0{\cdot}860 (T_{,,} \log_e P_{T_{,,}} - T_{,} \log_e P_{T_{,}}) 10^{-4} \text{ volt} \\ & + 0{\cdot}860 (T_{,} \log_e a\mu T_{,} - T_{,,} \log_e a\mu T_{,,}) 10^{-4} \text{ volt} + E_1'(T_{,} - T_{,,}) \dots \quad \text{(II')}.\end{aligned}$$

Equation (II') differs from the equation of Nernst by the term E_3 which I put $= E_1'(T_{,} - T_{,,})$, but while Nernst assumes that E_1 and E_3 remain unknown, and tries to eliminate them (*i.e.* their content), by the use of two different concentrations, we shall try to determine the value and content of these equations so as to get to the fundamental equation concerning the thermogalvanic system for any one concentration.

If $P_{T_{,}}$ and $P_{T_{,,}}$ are the solution pressures of the electrodes, they must follow a law analogous to Clausius' law for evaporation in a vacuum, *i.e.*, $\frac{dP}{dT} = \frac{-\rho + RT}{Tv}$ and therefore $\log_e P_{T_{,}} = \frac{\rho}{RT_{,}} + \log_e T_{,} + K$ and $\log_e P_{T_{,,}} = \frac{\rho}{RT_{,,}} + \log_e T_{,,} + K$.

Putting these values into equation I and II′ we get:—

$$\Sigma E = [0{\cdot}860\,(K - \log_e a\mu)10^{-4} + E'] \, (T_{,} - T_{,,}), \text{ instead of } (I');$$

$$\Sigma E = [0{\cdot}860\,(\log_e a\mu - K')\,10^{-4} + E'] \, (T_{,} - T_{,,}), \text{ instead of } (II'),$$

i.e., the E.M.F. of constant thermogalvanic cells reversible in respect of either cation or anion, must be directly proportional to the differences of temperature of the two plates in contact with the liquid. From the observations of Nernst and myself, it can be shown that this is actually the case. Hence we prove that:

(1) The thermogalvanic E.M.F. is directly proportional to the difference of temperature of the two places of contact of the plates with the liquid (deduced in two ways).

(2) The solution pressure of the electrodes follows a law similar to Clausius' law of evaporation.

(3) The law of Gibbs and Helmholtz giving the connection between the E.M.F. of a galvanic combination, the heat of reaction, and the temperature coefficient of the E.M.F., holds good for each of the two potentials separately, giving thus the connection between the electric potential differences of the given plate and solution, the heat of ionisation of the given plate, and the temperature coefficient of the value of this potential difference.

(7) A very detailed investigation of the E.M.F. in the dark showed that it is due to the formation of "gas batteries" through adhesion of gases in different concentrations to the plates, the degree of adhesion depending upon the state of the surface of the plate. The current polishes the plates, the amount of the gases adhering to them becomes thus more equal, and according to the equation $\pi = \frac{0{\cdot}0002T}{n_e} \log_e \frac{P_1}{P_2}$ the E.M.F. of the gas battery becomes smaller. From these we must distinguish gas batteries created under the action of light as the result of the chemical processes going on in the system under the action of the current—the separation of gas upon one electrode only, or of different gases on the two electrodes.

"Experiments on the Nature of the Opsonic Action of the Blood Serum."

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In a series of simple and convincing experiments Wright and Douglas* have shown that in phagocytosis so called, an important if not a cardinal *rôle* is played by the body humors, whereby they act upon the bacteria, thus rendering the latter an easy prey for the polynuclear leucocytes. The demonstration of this *opsonic* action of the serum or plasma was mainly brought about by testing separately and combined the body humors and the corpuscles which had been washed in salt solution. Contrary to general opinion, Wright and Douglas found that the leucocytes were capable of engulfing microbes only when the latter had been attacked by the serum or plasma. This attack on the microbe does not lead to the death of the latter, as sera may manifest a marked opsonic effect without being in the slightest degree bactericidal. Wright and Douglas found that the opsonic substance was more or less thermolabile, being destroyed in 10 to 15 minutes at a temperature of 60 to 65° C. In subsequent papers these authors have demonstrated that there is a definite type of immunity in which the blood fluids co-operate with the leucocytes to destroy the invading micro-organisms, this being different from the antitoxic and bactericidal types of immunity which have already been studied with completeness.

Technique.—The technique we have employed is that described by Wright, and for the most part the experiments were made with living cultures of *Staphylococcus albus* not more than 24 hours old. For accurate and uniform results it is essential that the emulsions of the cultures should be homogeneous, the bacteria being uniformly distributed and separated from each other. This is best obtained by shaking, and the subsequent application of the centrifuge. From their tendency to group themselves into masses, certain strains of staphylococci are unsuitable for determining the opsonic power of the serum. Where different bacterial emulsions are compared with each other it is essential that they should contain the same number of bacteria, a result best obtained by counting and diluting as required.† The leucocytes were obtained from the citrated blood of the authors and other human beings or from rabbits. The sera used were either of human or animal origin and were for the most part from normal individuals.

In all cases the proportion of serum, bacteria, and corpuscles was 3 : 1 : 3.

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* 'Roy. Soc. Proc.,' vols. 72 and 73.

† See Wright, 'Lancet,' July 4, 1902.

Effect of Heat upon Serum containing Opsonin.—Serum ceases to exert an opsonic effect upon bacteria after it has been heated in the water bath at 60 to 65° for 10 to 15′. In most cases the opsonic effect is totally abolished at this temperature, in a few cases, however, some slight effect can be witnessed, but this is mainly, if not entirely, due to traces of serum left attached to the leucocytes where those have been incompletely washed in normal salt solution.

Experiment.—Normal rabbit's serum (three parts), mixed with staphylococcus emulsion (one part), and washed human blood corpuscles (three parts). A portion of this was tested, the serum being unheated. Other portions were heated to 60° C. for varying periods. In each case a phagocytic count was made by numbering the cocci in fifty leucocytes and then striking the average per leucocyte.

					Cocci per leucocyte.
1 (Control).	Normal serum		+ cocci	+ corpuscles	= 14
2.	Serum heated to 60° C. for	3′	+ ,,	+ ,,	= 0
3.	,, ,,	6′	+ ,,	+ ,,	= 0
4.	,, ,,	9′	+ ,,	+ ,,	= 0
5.	,, ,,	12′	+ ,,	+ ,,	= 0
6.	,, ,,	15′	+ ,,	+ ,,	= 0

The opsonin can, however, be destroyed at even lower temperatures if the heat is prolonged.

Experiment.—Here the conditions of the Experiment were the same, with the exception that the serum was heated to 55° and 50° respectively instead of at 60° C.

						Cocci per leucocyte.
(1)	1 (Control).	Unheated serum		+ cocci	+ leucocytes	= 10·9
	2.	Serum heated to 55° C. for	30′	+ ,,	+ ,,	= 0·3
	3.	,, ,,	60′	+ ,,	+ ,,	= 0
(2)	1. (Control).	Unheated serum		+ cocci	+ corpuscles	= 13
	2.	Serum heated to 50° C. for	10′	+ ,,	+ ,,	= 3·4
	3.	,, ,,	15′	+ ,,	+ ,,	= 2·4
	4.	,, ,,	20′	+ ,,	+ ,,	= 2
	5.	,, ,,	25′	+ ,,	+ ,,	= 1
	6.	,, ,,	30′	+ ,,	+ ,,	= 1

Effect of Cold upon Opsonin.—Cold exerts little effect upon the opsonic power of the serum; even when immersed in ice water for 24 hours the opsonic value sinks about one-third. At ordinary temperatures the opsonin is remarkably stable, showing practically no diminution for 24 hours.

Effects of Exposure to Light.—In ordinary diffused daylight the opsonic power of the serum remains unaltered for many hours, but when exposed to bright sunlight for 3 hours a serum was seen to become less opsonic in the proportion of 10 : 7.

Are the opsonins, or are the leucocytes, the variable factors when the phagocytic power of different bloods is compared? For many years Metchnikoff has taught that the leucocyte is the dominant factor in phagocytosis. He has also emphasised the training of the leucocyte as the essential thing in immunity. The experiments we have made confirm the results already obtained by Wright and point to the conclusion that the leucocyte is indifferent, the variable in a series of bloods being the serum. In a first series of experiments the *leucocytes* derived from seven different persons were tested with respect to their phagocytic power, one and the same staphylococcic emulsion and one and the same serum (rabbit's) being used in each case.

In a second series the *sera* of the seven individuals whose corpuscles had been used in the above experiment were tested in respect of their opsonic power, one and the same suspension of cocci, and one and the same variety of leucocytes (derived from one of ourselves, W. B.) being employed throughout.

Experiment I.—Rabbit's serum mixed with emulsion of staphylococci and human leucocytes (from seven persons) in the proportion of 3 : 1 : 3. Phagocytic count obtained by counting the number of cocci in thirty-five polynuclear leucocytes and then calculating the number per leucocyte.

		Cocci per leucocyte.
1.	Rabbit's serum + cocci + corpuscles (of W. B., a normal male)	= 9·8
2.	,, + ,, ,, (of F. T., ,,)	= 9·3
3.	,, + ,, + ,, (of O. G., ,,)	= 9·7
4.	,, + ,, + ,, (of R. D., ,,)	= 9·6
5.	,, + ,, + ,, (of C. H., ,,)	= 9
6.	,, + ,, + ,, (of H. M., an anæmic female)	= 9·9
7.	,, + ,, + ,, (of S. M., male, facial acne)	= 9

Experiment II.—Various human sera + cocci + one kind of leucocytes from a normal male individual.

		Cocci per leucocyte.
1.	Serum of W. B. + cocci + corpuscles of W. B.	= 21·3
2.	,, F. T. + ,, + ,, ,,	= 20·3
3.	,, O. G. + ,, + ,, ,,	= 21·1
4.	,, R. D. + ,, + ,, ,,	= 20
5.	,, C. H. + ,, + ,, ,,	= 19·8
6.	,, H. M. + ,, + ,, ,,	= 15·5
7.	,, S. M. + ,, + ,, ,,	= 14

The possible objection that the human leucocytes would be injured in contact with rabbit's serum is disposed of by an experiment in which the phagocytic power of one serum, either human or rabbit's, was determined with both human and rabbit's leucocytes. Even in this case the leucocyte is largely an indifferent factor.

						Cocci per leucocyte.
1.	Rabbit's serum	+	staphylococci	+ rabbit's	leucocytes	= 10·3
2.	,,	+	,,	+ human	,,	= 18
3.	Human serum	+	,,	+ rabbit's	,,	= 19·5
4.	,,	+	,,	+ human	,,	= 17·6

The preponderating effect exerted by the serum as distinguished from the polynuclear leucocytes is again brought out strikingly in the following experiment. In this case the serum mixed with corpuscles of a normal individual (W. B.) is compared with the sera and the corpuscles of three advanced cases of facial lupus, the first of these cases (No. 2 and No. 5) being a wretchedly under-nourished girl of ten with very extensive facial lupus and large ulcerated tubercular sores on the hands. The test material in this experiment was an emulsion of tubercle bacilli, and the number of T. B. in 100 leucocytes was counted, and the average struck as usual.

					T. B. per leucocyte.
1.	Serum of normal individual	+	T. B. emulsion	+ leucocytes of normal individual	= 5·7
2.	,, ,,	+	,,	+ leucocytes of a lupus patient	= 5·4
3.	,, ,,	+	,,	+ ,, ,,	= 5·2
4.	,, ,,	+	,,	+ ,, ,,	= 5·3
5.	Serum of a lupus patient	+	,,	+ leucocytes of a normal individual	= 2·5
6.	,, ,,	+	,,	+ ,, ,,	= 2·4
7.	,, ,,	+	,,	+ ,, ,,	= 3·2

Expressing these relations as the opsonic index, we have—

No. 1 = 1·0 = (normal serum + normal leucocytes).
,, 2 = 0·94 = (,, + leucocytes from lupus patient).
,, 3 = 0·90 = (,, + ,, ,,).
,, 4 = 0·93 = (,, + ,, ,,).
,, 5 = 0·43 = (lupus serum + normal leucocytes).
,, 6 = 0·43 = (,, + ,,).
,, 7 = 0·56 = (,, + ,,).

On the Constitution of the Opsonic Body in the Serum.—The bacterial bodies already known to exist in the serum are referable to one of three classes, viz., antitoxins, agglutinins, lysins. The last of these are the most complex, as the lytic action occurs only after the coalition of two distinct elements, the complement which for the most part is thermolabile, and the immune body, which is thermostable. The agglutinins are of simpler constitution, although here special conditions of the agglutinating substance (the serum) and the agglutinable substance (the bacteria) must exist before agglutination is manifest. Temperatures above 70° C. applied either to the serum or to the bacteria suffice to inhibit the agglutination, although the agglutinin is apparently not entirely destroyed. In comparison with the lysins and agglutinins the antitoxins are believed to be relatively simple bodies. We have asked ourselves the question to which, if any, of these classes do the opsonins belong, and we have followed the usual methods of experimentation which have been utilised to determine the constitution of such antibodies. These experiments chiefly consist in determining the temperature at which the specific action is abolished, the temperatures at which the antibody enters into combination with the bacteria, and whether the action of heat is one of destruction or merely a conversion into some modification in which the specific action is no longer manifest.

Can the opsonin act on bacteria which have been subjected to high temperatures ?

Experiment 1.

Technique.—Emulsions of cultures of staphylococcus were placed in sealed glass tubes and subjected to temperatures of 100 to 134° C. for varying periods, the opsonic action of serum on such heated cultures being compared with that upon unheated emulsions.

Results.—

					Cocci per leucocyte.
1.	Normal human serum	+ unheated cocci		+ leucocytes	= 30
2.	,, ,,	+ cocci heated to	100° C. for 30′ +	,,	= 20
3.	,, ,,	+ ,, ,,	100° C. for 60′ +	,,	= 20
4.	,, ,,	+ ,, ,,	115° C. for 30′ +	,,	= 15
5.	,, ,,	+ ,, ,,	120° C. for 30′ +	,,	= 15

Experiment 2.

					Cocci per leucocyte.
1.	Human serum	+ unheated cocci		+ corpuscles	= 27
2.	,,	+ cocci heated to 100° C. for	½ hr. +	,,	= 17
3.	,,	+ ,, ,,	1 ,, +	,,	= 15
4.	,,	+ ,, ,,	1½ hrs. +	,,	= 12·9
5.	,,	+ ,, ,,	2½ ,, +	,,	= 13
6.	,,	+ ,, 134° C. for	1½ ,, +	,,	= 12·6

From these experiments it is apparent that there is a certain falling-off of the opsonic action when the cultures are kept at high temperatures for long periods, but even at 134° C. for 1½ hours the diminution in phagocytic power is about 50 per cent. It is possible, too, that the readings are really higher, as it is often very difficult to count the bacteria which have been subjected to such high temperatures on account of defective penetration of the stains employed.

Effect of heating to 60° C. a mixture of serum and cocci which have already been digested at 37° C. for 15′.

We have already seen that a temperature of 60° C. applied to the serum suffices to abolish its opsonic effect. Wright and Douglas showed, however, that if the serum were first brought into contact with bacteria at 37° C. for 15', and the mixture were then heated to 60° C. for 15', the cocci were picked up by leucocytes without difficulty. It was upon this experiment that they based their conclusion that the opsonin really acts upon the bacteria and does not merely stimulate the leucocyte. We have thought it important to determine whether prolonged heating at 60° C. of opsonised cocci can destroy the opsonic power so that these cocci cannot be picked up subsequently by leucocytes.

Experiment.

Technique.—Normal serum (three parts) mixed with staphylococcus emulsion (one part); mixture kept in water bath at 37° C. for 15'. This mixture, which is spoken of below as "opsonised cocci," was then distributed into a series of glass pipettes which were placed in the water bath at 60° C. for periods of 15' up to 5 hours. On removal from the water bath, four volumes of the "opsonised cocci" were mixed with three volumes of corpuscles at 37° C. for 15', and the phagocytic count made as usual. For comparison the phagocytic count of unheated serum + cocci, and of serum heated to 60° C. before being mixed with cocci, is added.

Results.—

						Cocci per leucocyte.
1.	Unheated serum (3 vols.)		+ cocci (1 vol.)	+ corpuscles (3 vols.)		= 23
2.	Serum heated to 60° C. for 15'		+ ,, ,,	+	,, ,,	= 0·1
3.	"Opsonised cocci" at 60° C. for	15' (4 vols.)		+	,, ,,	= 27
4.	,, ,,	30' ,,		+	,, ,,	= 28
5.	,, ,,	45' ,,		+	,, ,,	= 23
6.	,, ,,	60' ,,		+	,, ,,	= 24·5
7.	,, ,,	1½ hrs. ,,		+	,, ,,	= 23
8.	,, ,,	2 ,, ,,		+	,, ,,	= 23·5
9.	,, ,,	2½ ,, ,,		+	,, ,,	= 22
10.	,, ,,	3 ,, ,,		+	,, ,,	= 24
11.	,, ,,	5 ,, ,,		+	,, ,,	= 23·5

The experiment shows that some change is produced in the bacteria during the 15' exposure at 37° C. and the change is such that subsequent heating to 60° for even 5 hours is inoperative, this being very different to the effect of a preliminary heating of serum at 60° C. before admixture with bacterial emulsion.

Experiments on the rate of disappearance of opsonin from serum when the latter is brought into contact with cocci at 37° C. and at 0° C.

Experiment.

Technique.—Normal serum mixed with an equal volume of staphylococcus emulsion and then filled into a series of capsules. The capsules were sealed and placed in the water bath at 37° C. or in a mixture of ice and salt. After varying periods the capsules were removed and carefully centrifugalised for 1 hour, the clear supernatant fluid from each capsule being tested upon a fresh suspension of staphylococcus to see whether the opsonin had disappeared. As a control the opsonic power of normal serum in proper dilution is also added, likewise the opsonic power of serum which has been heated to 60° C. for 15′.

Results.—

							Cocci per leucocyte.
1.	(Control). Normal serum (3 parts)	+	cocci (1 part)	+	corpuscles (3 parts)	=	18·7
2.	(Control). Heated ,, ,,	+	,, ,,	+	,, ,,	=	0·1
3.	Supernatant fluid from capsule at 37° C. for 5′	+	,, ,,	+	,, ,,	=	0
4.	Ditto ditto ditto 10′	+	,, ,,	+	,, ,,	=	0
5.	Ditto ditto ditto 15′	+	,, ,,	+	,, ,,	=	0
6.	Ditto ditto ditto 30′	+	,, ,,	+	,, ,,	=	0
7.	Ditto ditto ditto 45′	+	,, ,,	+	,, ,,	=	0
8.	Ditto ditto at 0° C. for 10′	+	,, ,,	+	,, ,,	=	0
9.	Ditto ditto ,, 20′	+	,, ,,	+	,, ,,	=	0
10.	Ditto ditto ,, 30′	+	,, ,,	+	,, ,,	=	0
11.	Ditto ditto ,, 45′	+	,, ,,	+	,, ,,	=	0

The result is unequivocal; the opsonin had completely disappeared from the serum within 10′ both at 37° C. and at 0° C.

Experiments to Determine the Nature of the Opsonic Body, and its Mode of Action.—We have seen above, that when heated to 60° C., serum ceases to exert an opsonic effect. We have also seen that opsonin disappears from the serum when the latter is digested with bacteria at 37° C., or at 0° C. Is this disappearance due to destruction, or does the opsonin pass into some modification, in which an opsonic effect is not visible? Is the opsonin a simple, or a complex structure?

Experiment.

Technique.—(1) Normal serum was digested with an equal quantity of emulsion of cocci at 37° C. for 15′. After digestion, mixture was centrifugalised for ¾ hour. In this way a clear supernatant fluid (A) was separated from a deposit of cocci (A′).

(2) Normal serum was digested with an equal quantity of emulsion of cocci at 0° C. for 15′, centrifugalised as above, and separated into a supernatant fluid (B) and a deposit (B′).

As the serum was mixed with equal quantity of cocci, the controls made with normal serum and "normal" cocci are given in their appropriate dilutions, which were made with 0·85 per cent. saline. The term "normal" is applied to cocci which have not been treated in any way.

Results.—

				Cocci per leucocyte.
1 (Control).	Normal serum (2-fold dilution)	+ "normal" cocci	+ corpuscles	= 25
2	,, ,, (4- ,,)	+ ,,	+ ,,	= 17
3.	Fluid A	+ ,,	+ ,,	= 1
4.	,, B	+ ,,	+ ,,	= 2·5
5.	,, A	+ cocci B′	+ ,,	= 27
6.	,, A + B	+ "normal" cocci	+ ,,	= 3
7 (Control).	Normal serum (undiluted)	+ ,,	+ ,,	= 31
8.	,, ,,	+ cocci A′	+ ,,	= 28
9.	,, ,,	+ ,, B′	+ ,,	= 26·5

This experiment again shows the disappearance of the opsonin from the serum at 37° and 0° C. It also shows (Nos. 8 and 9) that the opsonin has passed into the cocci (A′ and B′).

Experiment 2.

In this experiment an attempt was made to determine whether at 0° C. a complement-like body could be separated out, which, with heated serum, would exert an opsonic effect.

Technique.—1. Normal serum mixed with emulsion of cocci, in equal parts, at 0° C. for 15′. The mixture was then centrifugalised, and separated into a supernatant fluid (A) and a deposit (A′).

2. Serum *heated* to 60° C. for 15′, mixed with cocci ($\overline{\text{aa}}$), and placed at 0° C. for 15′. It was then centrifugalised, and separated into a supernatant fluid (B), and a deposit (B′). Controls were supplied by normal serum (in appropriate dilutions), digested with "normal" cocci and corpuscles at 37° C., and heated serum under the same conditions.

Results.—

				Cocci per leucocyte.
1 (Control).	Normal serum (2-fold dilution)	+ "normal" cocci	+ corpuscles	= 25
2 ,,	,, (4-fold ,,)	+ ,,	+ ,,	= 18
3 ,,	Serum heated to 60° C. for 15′	+ ,,	+ ,,	= 2
4.	Fluid A + heated serum ($\overline{\text{aa}}$)	+ ,,	+ ,,	= 3
5.	Fluid A	+ ,,	+ ,,	= 3
6.		cocci A′	+ ,,	= 22
7.		cocci B′	,,	= 4

Remarks.—This experiment shows that the opsonin is very different in type from a lysin, as apparently no complement-like body remains in the supernatant fluid after the serum has been digested at 0° C. The low reading in the case of the deposit B′ would also lead to the supposition that the action of heat at 60° has been to destroy the opsonin altogether. This supposition is confirmed by the following experiment.

If heated serum is unable to exert an opsonic action on staphylococci, are the latter, when digested with heated serum, capable of being opsonised by unheated serum?

Experiment.

Technique.—Normal serum was heated to 60° C. for 15′, then mixed with an equal quantity of staphylococcus emulsion, and digested at 37° C. for 15′, the deposit of cocci (A) being then removed by the centrifuge.

The deposit (A) was then divided into two parts, one being reserved for the opsonic test, the other being mixed with *normal* serum. The mixture was digested for 30′; the centrifuge was then applied, so as to separate a supernatant fluid (B) from a deposit of cocci (B′).

Results.—

				Cocci per leucocyte.
1 (Control).	Normal serum	+ normal cocci	+ corpuscles	= 18·6
2.	,, ,, *(2-fold dilution)*	+ ,,	+ ,,	= 16
3.	,, Heated serum	+ ,,	+ ,,	= 0·5
4.	Normal serum	+ cocci A	+ ,,	= 15·5
5.	Fluid B	+ normal cocci	+ ,,	= 0·4
6.		cocci B′	+ ,,	= 15

This experiment bears out the suggestion above, that heat destroys the opsonin. The cocci (A) having been quite uninfluenced by the heated serum, were capable of being opsonised by normal serum, and they were further, as shown in No 5, capable of abstracting all the opsonin out of normal serum. After being acted on by the normal serum, the mere addition of corpuscles demonstrated that they had been acted upon by the opsonin (No. 6).

Results.—

1. Opsonin is present in the normal serum.
2. Opsonin is thermolabile.
3. It rapidly disappears from the serum when the latter is mixed with bacteria at 37° C. or at 0° C.
4. After the opsonin has united with the bacteria the mixture of serum and cocci can be heated to 60° C. for long periods without abolition of the opsonic effect.
5. The leucocyte is practically an indifferent factor when the phagocytic power of different bloods is compared.
6. The capacity of bacterial emulsions for extracting opsonin from the serum is only slightly diminished by subjecting these emulsions to very high temperatures over prolonged periods.
7. The action of heat is to destroy the opsonin, and not merely to convert it into a non-opsonisable modification.
8. The opsonin is not identical with any of the anti-bodies hitherto discovered in the serum.
9. The opsonin is of relatively simple constitution; where these experiments cover the same ground as those of Wright and Douglas, the observations of these authors are confirmed.

"Note on the Effects produced on Rats by the Trypanosomata of Gambia Fever and Sleeping Sickness." By H. G. PLIMMER, F.L.S. Communicated by Dr. C. J. MARTIN, F.R.S. Received December 1, 1904,—Read January 19, 1905.

(From the Laboratories of the Lister Institute of Preventive Medicine.)

The following observations are of interest in connection with the view that Gambia Fever may be the early stage of the disease which ends as Sleeping Sickness, which is held by some: and with the question of the causal relationship of the Trypanosoma found in Sleeping Sickness to the disease.

The Trypanosomata used in the experiments mentioned below were given to me by Col. Bruce, F.R.S.; that of Gambia Fever having been taken from a monkey inoculated in Africa from a native boy suffering from Gambia Fever, and that of Sleeping Sickness from a monkey inoculated in Africa from a case of this disease.

Gambia Fever.

Fourteen rats were inoculated with the Trypanosoma of Gambia Fever at intervals between December 11, 1903, when I received the first rat from Col. Bruce, and August 24, 1904, all of which are dead. In each case the Trypanosomata were present in the blood, the first appearance of them there being about four weeks after inoculation: and towards the end of the disease they were present in large numbers. The average time between inoculation and death was two months and twelve days. In each case the spleen was enormously enlarged; there was considerable hyperplasia of the follicles, and the pulp was congested in varying degrees. There was also marked hyperplasia of the lymphatic glands, especially of those of the mesenteric and mediastinal areas. There was congestion of the liver, with cloudy swelling of its epithelium, and the same condition in a lesser degree was found in the kidney. In no case was there any paralysis, or any nervous symptoms, except that just before death the animals became heavy and apathetic. *Post mortem* the capillaries of the brain contained large numbers of the organisms.

Sleeping Sickness.

Three rats were inoculated on December 1, 1903, from a monkey which had been brought home by Col. Bruce from Africa after inoculation with cerebro-spinal fluid from a case of Sleeping Sickness. At no time were any Trypanosomata found in the blood of these rats, even after it had been centrifugalised *post mortem.* One rat became paralysed in both hind legs on May 12, 1904, and died on May 23; the second became paralysed similarly on August 2, and died on August 30; and the third became paralysed on August 28, and died on September 8. On *post mortem* examination no naked-eye lesions of any organ were found, and the spleens were not enlarged. The blood was citrated and centrifugalised, and the organs were mashed and washed with normal salt solution and centrifugalised, but in no case were any Trypanosomata found. Portions of the extracts of liver, spleen, and spinal cord were injected into other rats, but up to the present these show no sign of illness. In the mashed spinal cord of each of these rats the characteristic Trypanosomata were found in small numbers, but none were found in the brains which were examined in the same way. The three rats were of the same kind, black and white; and the youngest of the three died first and the eldest last.

(1) These experiments go to show that the two diseases—Gambia Fever and Sleeping Sickness—from which the organisms were obtained, are distinct; the duration of the diseases, the symptoms, and the *post mortem* appearances being quite different.

It is evident that these two organisms are quite separate and distinct, as their different effects on similar animals indicates; moreover, they are also morphologically distinct when grown in similar animals, that of Gambia Fever being longer, generally larger, and more easily stainable than the stumpy, large-vacuoled, badly staining Trypanosoma of Sleeping Sickness.

The fact of the clinical observation that Gambia Fever not infrequently appears to terminate with all the symptoms of Sleeping Sickness may quite possibly be explained by a double infection. For, in both rats and monkeys the one Trypanosoma does not interfere with the other, but the more active organism—that of Gambia Fever in the cases of rats and monkeys—kills in about the same time, whether inoculated before, with, or after that of Sleeping Sickness.

(2) There can be no question, from the above experiments, of the susceptibility of the rat to the Trypanosoma of Sleeping Sickness.

(3) These experiments show that the inoculation of the Trypanosoma of Sleeping Sickness into rats gives rise to no obvious symptoms for many months, nor are Trypanosomata discoverable in the blood by microscopic examination. But, after a period of from six to nine months paraplegia occurs, leading to the death of the animal; and *post mortem* the organisms are found only in the spinal cord. The organisms are thus in rats, as sometimes in man, entirely confined to the nervous system; whereas in monkeys they are, in my experience, always generalised at some period of the disease.

Addendum, January 19, 1905.—The three rats inoculated on August 30, 1904, with extract of spinal cord have become paraplegic: one on December 14, 1904, one on January 2, 1905, and the third on January 11, 1905. No Trypanosomata have been seen in the blood of these animals, and, apart from paralysis of the hind limbs, they show no signs of ill health.

The spinal cord shows amœboid forms of the Trypanosomata in its tissue, and a considerable cellular exudation around the vessels; this lesion Dr. Mott found to be characteristic of cases of human Sleeping Sickness, and it is not found in monkeys, which have been the animals principally used in experimental work on this disease.

"Further Histological Studies on the Localisation of Cerebral Function.—The Brains of *Felis*, *Canis*, and *Sus* compared with that of *Homo*."[*] By ALFRED WALTER CAMPBELL, M.D. Communicated by Professor SHERRINGTON, F.R.S. Received December 3, 1904,—Read January 19, 1905.

(Abstract.)

The present study is founded on an exhaustive examination of the cerebral cortex of *Felis domesticus*, *Canis familiaris*, and *Sus communis*, conducted on lines similar to those followed in the original work.

A recurrence in the lower mammal of distinctive types of cortex, akin to those recognised in the human brain, has allowed a subdivision of the surface into the following areas:—

Crucial or motor; postcrucial or sensory; parietal; visual; ectosylvian; limbic; rhinic; extrarhinic; frontal.

By a study of the distribution of these areas many functional analogies and structural homologies, previously unknown or misinterpreted, are made clear.

Crucial or Motor Area.—Giant cells of Betz characterise the motor cortex, but these elements appear not to be so highly specialised in *Sus* as in *Felis* and *Canis*. Such cells reside in what we may call the cruciate zone, and it is maintained that this field is functionally and morphologically akin to the motor area, as defined by Professors Sherrington and Grünbaum in the anthropoid ape, and by myself in man. It is held that a small indentation, called the "compensatory ansate" sulcus, and the sulcus coronalis are respectively interchangeable with the upper and lower constituents of the primate fissure of Rolando, chiefly because they, like the fissure of Rolando, limit the

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[*] This paper is an addendum to the work presented to the Royal Society in November, 1903 (see 'Proceedings,' vol. 72, p. 488). The complete work will be published shortly in full by the Cambridge University Press, by aid of a subsidy from the Royal Society.

motor area on the parietal side. In man and the man-like ape, an unnamed but constant fissuret, situated on the paracentral lobule, immediately below and in front of the upper extremity of the fissure of Rolando, is looked upon as the homologue of the sulcus cruciatus.

Visual Area.—Showing how greatly the lower mammal relies on sight in the contest for survival, quite one-sixth of the brain surface is allotted to visual cortex. Architecturally it is astonishing how closely the human plan is followed. The lessons in homology learned are, that the "true calcarine" fissure (Elliot Smith's nomenclature) of lower mammals is the antecedent of the anterior calcarine fissure or "stem" of *Homo*, that the intercalary sulcus does not develop into the calloso-marginal of man, but undergoes retrograde changes, that the posterior calcarine fissure may continue as such, and that the suprasplenial sulcus of *Canis* and *Felis* (the so-called "lateral" sulcus of *Sus*) is the derivative of the human fissura extrema of Seitz (the Simian "sulcus intrastriatus lateralis"). The research throws no light on the problem of the "Affenspalte."

Postcrucial or Sensory Area.—The postcrucial or sensory field forms a morphological buffer to the crucial or motor, and is maintained to be the homologue and analogue of the postcentral area in primates.

Lobus Pyriformis and Hippocampal Region.—The variations in distribution of the different types of cortex found hereabouts are contrasted in the microsmatic and macrosmatic brain.

Limbic Area.—It is found that types of cortex akin to those recognised in man are repeated in the lower mammal. The genual fissure is taken as the homologue of the calloso-marginal.

Parietal Area.—Histology suggests that this field is the forerunner of the parietal area in *Homo*, and that its cortex is older, in the sense of phylogeny, than frontal cortex. Support is given to the assumption that the lateral sulcus, as seen in most mammals, is the antecedent of the intraparietal sulcus of primates. In *Sus*, the so-called "suprasylvian" sulcus is really the lateral, the true suprasylvian sulcus being both placed at a lower level and rudimentary.

Ectosylvian Region.—Out of the ectosylvian region of lower mammals is developed the sylvian region, including the insula, and much of the temporal lobe of primates. A small field investing the so-called fissure of Sylvius of lower mammals appears to be the analogue of the "audito-sensory" area of man and the homologue of the transverse temporal gyri. From this as a basis important deductions can be drawn.

Frontal Lobe.—The types of cortex which characterise the frontal lobe in man are not represented in lower mammals.

Some General Conclusions.—The stability of the architectural plan of any given field of cortex is directly related to the phylogenetic age of that cortex and to the importance, as a means to survival, of the function it subserves.

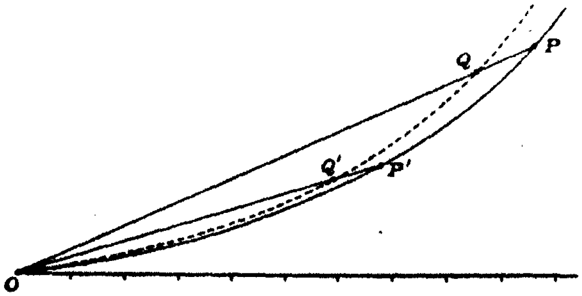
The human brain shows signs of having expanded more decisively in some parts than in others, yet that expansion, if we except the visual and olfactory areas, has been general in kind.

By super-imposing on our cerebral plans drawn from naked-eye inspection others giving the results of histological examination, this as a preliminary to the final localisation of function by the physiologist and workers in other departments, all existing doubt on various homologies may be removed.

"Exterior Ballistics.—'Error of the Day,' and other Corrections to Naval Range-tables." By Professor GEORGE FORBES, F.R.S.

Received December 19, 1904,—Read January 26, 1905.

One of the most common problems that meet artillerists is that of correcting for retardation caused by air-resistance, this being proportional to the air-density. The published range-tables, as calculated for any type of gun with given weight and form of shot, and given charge of powder, are based on trials with different elevations when the range and time of flight are measured directly. The range-tables are calculated from the experiments by making corrections for muzzle velocity and for air density. The problem now before us is to find a simple rule for deducing from the published range-table another range-table with a different air-density.



Abscissæ represent ranges.
Ordinates represent elevations.
PP' range table elevations at normal air density.
QQ' „ with air density increased 10 per cent.
QP = $\frac{1}{11}$ OP, Q'P' = $\frac{1}{11}$ OP'.

The solution of this problem, for flat trajectories at least, is extremely neat when stated geometrically. Draw a curve in which abscissæ are ranges and ordinates are the elevations of the range-table.

To draw a similar curve for air-density increased in the ratio $m : 1$ proceed as follows:—From the origin of co-ordinates O draw straight lines to points P, P′, etc., on the range-table curve. In these lines take points Q, Q′, etc., so that $OP/OQ = OP'/OQ' = \text{etc.} = m$. Then the locus of Q is the new curve.

Stated verbally the rule is:—To make a range-table for x per cent. increase of air-density (or x per cent. increase of retardation due to diameter and weight of shot), diminish each elevation and corresponding range by x per cent. The elevations thus found are correct for the ranges thus found with the new air-density. The time of flight is diminished by x per cent. The remaining velocity found in the range-table is the same for the new range-table at the altered range.

Adopting the usual notation for exterior ballistics—

X is the range in feet; V is the muzzle velocity.
$C = w/nd^2$.
w = weight of projectile; d = diameter of projectile.
n = a constant depending on form of shot and air-density.
v_1 = remaining velocity.
v_0 = velocity at the vertex of trajectory.
t = time of flight; ϕ = elevation.

Certain functions of velocity have been calculated and tabulated. These are S (v), T (v), D (v); and the following are three well-known equations:—

$$S(v_1) = S(V) - \frac{X}{C} \quad \ldots\ldots\ldots\ldots \quad (1).$$

From this we find v_1 from the tables;

$$t = C\{T(V) - T(v_1)\} \quad \ldots\ldots\ldots\ldots \quad (2).$$

Taking T (V), and T (v_1), from the tables, we know t.

Now it is always assumed that for elevations up to 15° the vertex of trajectory is reached in half of the time of flight. Hence

$$T(v_0) = T(V) - \frac{\frac{1}{2}t}{C},$$

whence we find v_0 from the tables, which also give us the values D (V) and D (v_0) in the third equation

$$\phi = C\{D(V) - D(v_0)\} \quad \ldots\ldots\ldots\ldots \quad (3).$$

If the air-density be now increased in the ratio m to 1, and we use letters with accents for the new conditions,

$$C' = \frac{w}{mnd^2} = \frac{C}{m}.$$

Let us find the elevation for a range X′ where

$$X' = X/m. \qquad \text{Then } X'/C' = X/C.$$

Thus in (1) $X'/C' = X/C$, and V is unchanged. Therefore v_1 remains unchanged, or $v'_1 = v_1$. And in (2) $t'/t = c'/c = 1/m$; or $t' = t/m$.

Also v_0' is found from the equation

$$T(v'_0) = T(V) - \frac{\frac{1}{2}t'}{C'} = T(V) - \frac{\frac{1}{2}t}{C} = T(v_0).$$

Therefore $$v'_0 = v_0.$$

Again, in (3)

$$\phi' = C'\{D(V) - D(v'_0)\} = C'\{D(V) - D(v_0)\} = \frac{C'}{C} \cdot \phi = \frac{\phi}{m}.$$

It appears then that if the air-density be increased m-fold and the range diminished m-fold, the elevation and time of flight must be diminished m-fold, but the remaining velocity is the same.

The above is founded on Niven's formulæ, but those of Siacci and Mayevski lead to the same result.

Another important correction is that of muzzle velocity, which depends upon age of gun and on temperature and nature of explosive. If there were no air-resistance the ordinary formulæ tell us that the elevation for any range varies inversely as the square of the muzzle velocity. I find empirically, by comparison of range-tables based on experiments with different muzzle velocities, that the same law holds over a very considerable range of muzzle velocities up to elevations of 10° at least. This has been tested with the Naval guns of 13·5 inch, 12 inch, 9·2 inch, and 6 inch diameters.

We can now subject these two laws (air-resistance and muzzle velocity) to a very severe test. Take the Naval range-table for 12-inch B.L. Gun, Mark IX, with an 850 lb. shot and muzzle velocity 2433 feet per second and from it calculate (by the two laws above) a range-table for the 6-inch Q.F. gun, Marks III, IV, and VI, with a 100 lb. shot and muzzle velocity 1960 feet per second.

To do this, note that the ratio of

$$\frac{\text{Diameter}^2}{\text{Weight}} \text{ is } \frac{12^2}{6^2} \times \frac{100}{850} = \frac{1}{0 \cdot 4706}.$$

Hence we must multiply the ranges and elevations of the 12-inch gun by 0·4706. We must further multiply the new elevations by 1·540, the ratio of the squares of muzzle velocities. The following table shows the results, and a comparison with the data for the 6-inch gun from the Addenda to Naval Range-Tables, and the differences :—

From range-tables, 12-inch gun. M.V. = 2483 f.s.		Calculated, 6-inch gun. M.V. = 1960 f.s.		From addenda elevation for new range.	Difference.
Range.	Elevation.	New range.	Elevation.	Elevation.	
yards.	° ′	yards.	° ′	° ′	′
2000	1 1	941	0 44	0 45	−1
4000	2 10	1882	1 34	1 38	−4
6000	3 37	2824	2 37	2 39	−2
8000	5 26	3765	3 56	3 54	+2
10000	7 33	4706	5 28	5 24	+4

It need hardly be said that the agreement is sufficient for all practical purposes.

An additional fact, of considerable practical importance, is that there is a very simple approximation to the true correction for elevation due to air-density, obtained by taking it as being a constant multiplied by the product of elevation and range, and percentage variation from the normal air-density. The constant varies with the type of gun and with full, or half, charge; but remains the same for all ranges. Thus with the 6-inch gun, Mark VII, the correction at full charge is $\frac{\text{range} \times \text{elevation}}{1,000,000}$, and at half charge it is $\frac{\text{range} \times \text{elevation}}{1,250,000}$. Curiously enough the same formula, with a different constant, gives the correction, at all ranges, to the elevation, due to rate of change of distance during the time of flight of the shot.

These empirical laws, combined with the muzzle velocity law already mentioned, have led to the design of a most simple arrangement of gun-sights corrected for the individual error of the gun due to wear, and for the error of the day due to temperatures of cordite and of the air, and to barometric pressure, which can be worked by the act of using the range-finder, and automatically corrects for time of flight with changing range.

"The Theory of Symmetrical Optical Objectives.—Part II." By S. D. Chalmers, B.A., St. John's College, Cambridge, M.A. Sydney. Communicated by Professor Larmor, Sec. R.S.

Received January 3,—Read January 26, 1905.

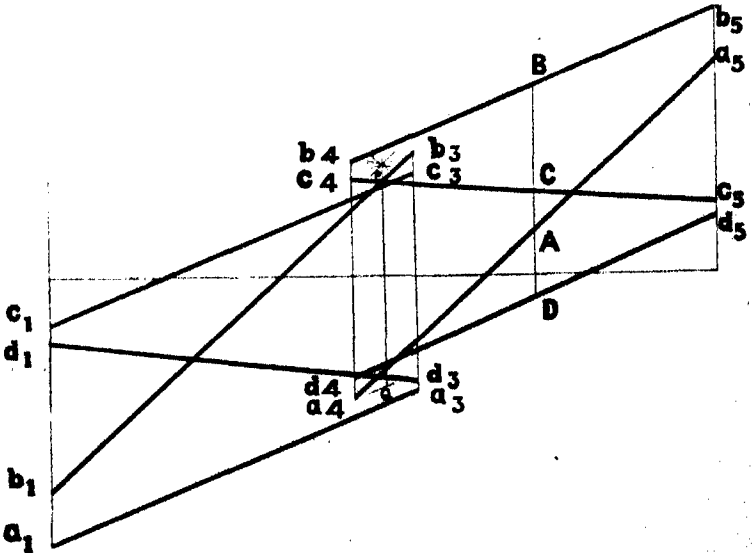
As regards the defects which depend only on those terms in the characteristic function T, that were examined in Part I,* the results of that paper would justify the practice of correcting a single component—the back one—for astigmatism and spherical aberration, provided due attention be paid to the securing, at least approximately, *of the condition for no distortion.*

But for the values of aperture-ratio and angular field, that obtain in practical systems, the terms of higher orders in T introduce important aberrations, and it is interesting to examine how far the conclusions stated in Part I* are justified in the case of practical systems.

In most cases the discussion can be effected by the use of geometrical relations, it being assumed—as is generally the case in practice—that the stop is well within the focus of the single lens and that its virtual image, formed by either component, is near the actual position of the stop.

In the first place we consider only those rays which lie wholly in one plane. In fig. 1, (5) is the focal plane of the back component,

FIG. 1.



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* 'Roy. Soc. Proc.,' vol. 72, June 18, 1903.

(2) the plane of the stop, (3) and (4) its images with respect to the front and back components, and (1) the plane symmetrical to (5); P and Q are two points on the stop equidistant from the centre, *a* and *b* two parallel rays through these points, *c* and *d* another pair of parallel rays through these points; the intersections of these rays with the planes 1, 3, 4, and 5, being a_1, a_3, a_4, a_5, b_1, etc. The ray *d* is chosen so that b_4, b_5 is parallel to d_4d_5, then by symmetry it is evident that c_1c_3 is parallel to a_1a_3. It is also evident that the planes 3 and 4, being images of 2, are in every way similar; hence they are the principal planes of the whole system, and the focal plane of the combined system is mid-way between 4 and 5. Let the various rays intersect this plane in A, B, C, and D.

The curvature error* of the combined system can be measured by CA, less the effects due to spherical aberration, where CA evidently

$$= \tfrac{1}{2}\,(c_4a_4 - c_5a_5)$$

but, since b_4b_5 is parallel to d_4d_5,

$$\mathrm{CA} = \tfrac{1}{2}\,\{(b_5a_5 + c_5d_5) - b_4c_4 - a_4d_4)\}\,.$$

Thus omitting effects of spherical aberration in both cases, it is evident that the curvature error for an angle ω and aperture angle 2α is the mean of the curvature errors for the single system for the angles $(\omega_0 + \tfrac{1}{2}\alpha)$,and $(\omega_0 - \tfrac{1}{2}\alpha)$, where $\omega - \omega_0$ represents the angular value of the distortion of the single lens, together with the portion of $\tfrac{1}{2}\,(b_4c_4 - a_4d_4)$, which is not common to all angles.

When the meridianal astigmatic curve is drawn as usual—the focal lengths being unreduced and the abscissæ representing *angular* field—the ordinates for the combined system will be one-half of those for the single system, subject to the corrections from terms corresponding to $\tfrac{1}{2}\,(b_4c_4 - a_4d_4)$.

To appreciate the value of the latter expression draw through P the rays *a*, *d*, symmetrical to *a* and *d* with respect to the axis, then $b_4c_4 - a_4d_4 = c_4a'_4 - c_4d'_4$, and since the angles between *b* and *a*, and *c* and *d*, are equal, this quantity will, in general, be small when the stop and its image are close together.

To examine the spherical aberration let c_4c_5 be parallel to the axis, a_4a_5 also parallel to the axis, then d_1d_3 and b_1b_3 are also parallel to the axis (fig. 2). The spherical aberration of the whole system is

$$\mathrm{DB} = \tfrac{1}{2}\,(b_5d_5 - b_4d_4)\,;$$

but $$c_4a_4 = c_5a_5,$$

therefore $$\mathrm{DB} = \tfrac{1}{2}\,\{c_5d_5 + a_5b_5 - (c_4b_4 + a_4d_4)\}\,.$$

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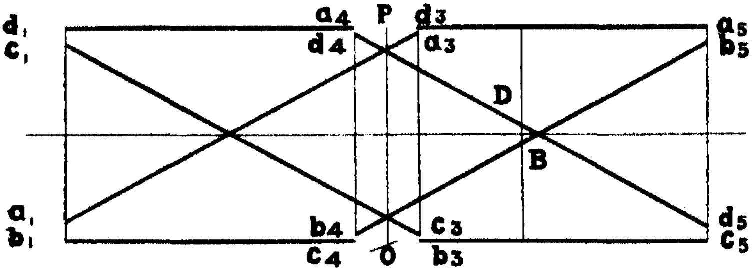
* This term is used for the defect due to the parallel rays through P and Q not intersecting on the focal plane, the effects of spherical aberration being allowed for.

Thus, if the single system be corrected for spherical aberration and curvature, the spherical aberration of the combined system is given by $\frac{1}{2}(c_4 b_4 + a_4 d_4)$. It is evident that this quantity will also be very small.

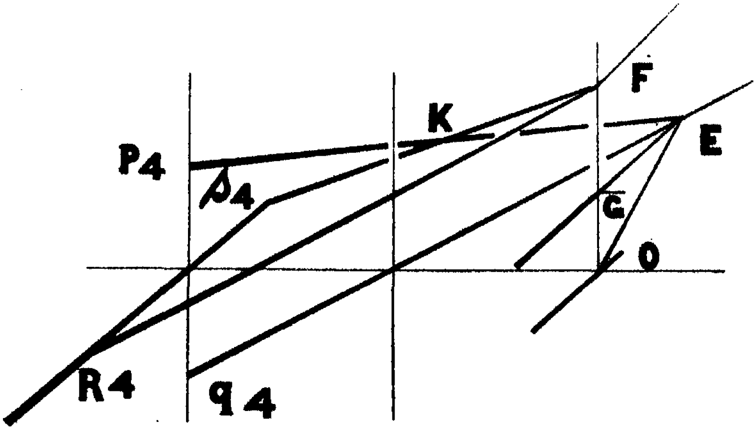
FIG. 2.



These results can be extended to the case of rays which do not lie wholly in one plane. It will be assumed that the image of the stop formed by one member is perfect, the errors thus introduced being of the same nature as those discussed before.

Let PQ and RS (fig. 3) be two diameters of the stop, their image

FIG. 3.



points in the plane 4 being $p_4\ q_4\ r_4\ s_4$; let parallel rays a and b pass through p_4 and q_4 respectively, and let the axial plane parallel to them cut plane 5 in OE; similarly parallel rays c and d pass through r_4 and s_4 and are parallel to the axial plane which cuts 5 in OF.

It being assumed that these pairs of rays intersect on the focal plane 5, the rays a and b will intersect on OE, say at E, and similarly *c* and *d* on OF at F. Through E draw EG parallel to RS, cutting OF in G. Now the rays *a b c* and *d* can be chosen so that EG = GF = $\frac{1}{2}$PQ. It is now evident from the figure that Fr_4 is parallel to Eq_4 and that Fs_4 and Ep_4 intersect in *k* on the plane mid-way between 4 and 5, which is the focal plane of the combined system.

But by symmetry the rays *b* and *c* in the second medium correspond to *a* and *d* in the first; hence the parallel rays *a* and *d* intersect on the focal plane of the combined system, but as RS is inclined at any angle to PQ all other rays parallel to *a* and *d* will also intersect at the same point.

Thus we have shown that, subject to the errors introduced by the want of correspondence of the stop and its image, the combined system is completely corrected for astigmatism, curvature of field, and spherical aberration, provided the back component is so corrected. This want of correspondence introduces some slight errors, but in practical systems these are almost negligible.

These conclusions accord very well with the deductions made by Dr. W. Zschokke, from the results of calculating the paths of rays through the various Goerz double symmetrical lenses.

"Note on the Cause of the Period of Chemical Induction in the Union of Hydrogen and Chlorine." By D. L. CHAPMAN and C. H. BURGESS, Demonstrators in Chemistry in the University of Manchester. Communicated by Professor H. B. DIXON, F.R.S. Received January 14,—Read January 26, 1905.

The induction period, which, in certain circumstances, is observed when a mixture of hydrogen and chlorine is exposed to light, has been commonly attributed to the preliminary formation of an unstable intermediate compound. The authors have for some time held that this view does not accord with the observed facts. This contention is confirmed by recent experiments, which have established that the phenomenon in question is due to the presence in the gas (or in the aqueous solution in contact with it) of substances capable of reacting with chlorine.

At an early stage in the investigation it was proved that the retardation of chemical action did not depend on any condition of the hydrogen, thus making it only necessary to consider the condition of the chlorine itself and of the other substances immediately in contact with it.

Water, and particularly solutions of salts in water, possess the power of rendering active chlorine inactive towards hydrogen. On long contact with chlorine in the presence of light, or on boiling with chlorine, these solutions lose this property even after subsequent removal of the chlorine by exhaustion. Numerous experiments have recently been made in order to find out if these solutions recover their power of rendering chlorine inactive, and it has been found that the only method of effecting this is by the introduction of substances which react with chlorine. Of the compounds investigated the most efficient to use for this purpose is ammonia, minute traces of which are capable of preventing the action between hydrogen and chlorine for a period of time many times longer than had been previously observed. Sulphur dioxide acts in the same sense as ammonia, but it is more easily removed on exposure to light.

It has been hitherto supposed that an active mixture of hydrogen and chlorine, after standing in the dark for several hours, returned to its original inactive condition. If this were really the case it would be an objection to the view that the induction period is due to the presence of impurities. By the employment of a quartz actinometer we have, however, succeeded in showing that no decay of activity takes place; and, after keeping the mixture for days in the dark, the gases immediately combine on exposure to light—without any period of gradual acceleration.

"On the Modulus of Torsional Rigidity of Quartz Fibres and its Temperature Coefficient." By FRANK HORTON, D.Sc., B.A., St. John's College, Cambridge, late Mackinnon Student. Communicated by Professor J. J. THOMSON, F.R.S. Received December 15, 1904,—Read January 26, 1905.

[Abstract.]

The author recently had the honour of reading to the Society the results of some experiments in which a new method of timing by means of "coincidences"—a method devised by Professor Poynting—was applied to an investigation of the effects of changes of temperature on the modulus of torsional rigidity of metal wires. It seemed desirable to repeat similar experiments with quartz fibres, seeing that now they are almost universally employed as suspensions in torsion instruments where accuracy is required.

The fibres experimented on were prepared from different crystals of quartz, and care was taken in their manufacture so as to obtain them free from air bubbles and of circular cross-section. The investigation was divided into three parts:

(1) The determination of the absolute value of the torsion modulus.

(2) The variation of the modulus over a range of temperature from 15° C. to 100° C.

(3) The variation of the modulus between 20° C. and 1000° C.

In the determination of the absolute value of the modulus, it is necessary to find the radius of the fibres used. The method adopted for this purpose consists of measuring the circumference of the fibre by rolling a small length of it between two fine glass capillary tubes and counting the number of revolutions it makes in travelling a distance of 5 mm. With practice, this method was made to give very good results; a fibre of diameter 0·001 cm. being measured to 0·01 per cent.

The results of experiments on six fibres gave numbers for the modulus of rigidity in very good agreement, showing that the rigidity of quartz is practically constant, and does not vary in different specimens as in the case of metal wires. The mean value obtained for the modulus of rigidity at 15° C. was

$$3{\cdot}001 \times 10^{11} \text{ dynes per sq. cm.}$$

The results showed that this value is independent of the longitudinal stress to which the fibres are subjected, so long as this is not greater than that which they are usually required to bear when used as suspensions in measuring instruments.

In the second part of the research, observations were made on several fibres at temperatures approximately 15° C., 35° C., 55° C., 75° C., and 100° C. In every case the modulus of rigidity was found to increase as a linear function of the temperature, but the values obtained for the temperature coefficient of the modulus were considerably different. The mean value was + 0·0001235, but the experiments show that this is far from constant in different specimens of quartz, its variations being much greater than those of the modulus of rigidity itself. It was found that the fibres became slightly more rigid as time went on, the rate of increase of rigidity being greater at the higher temperatures. This is probably due to a gradual annealing of the fibre, the annealing consisting in an easing of the structure from contraction strains.

In addition to the determination of the periods of torsional vibration, observations of the logarithmic decrements of the amplitudes of the oscillations were taken at each temperature. Fibres were also made to vibrate in an atmosphere of hydrogen, and the logarithmic decrements were again observed. From the values thus found, and the known ratio of the viscosities of air and hydrogen, a measure of the internal friction of the fibre was obtained. It was found that the internal friction of the fibres was very small, only about 2·5 per cent. of the observed logarithmic decrement at 15° C. being due to that cause, and that it remained roughly constant when the temperature of the fibre was raised from 15° C. to 100° C.

A series of observations was taken to ascertain the manner in which the logarithmic decrement, and the torsional period varied with the amplitude of vibration, amplitudes between 14′ and 10° being used. It was found that both the logarithmic decrement and the torsional period remained constant within these limits. In this respect quartz differs from metal wires, in which it was found that both the internal friction and the period of torsional vibration increased with the amplitude of oscillation.

In the experiments between 20° C. and 1000° C. the fibres used were rather thick and were suspended inside a platinum tube which was heated electrically, and which could be maintained at any desired temperature. Observations were taken at intervals of about 50° C., and the temperature of the tube was obtained by means of a thermo-junction of wires of platinum and rhodo-platinum. It was found that the modulus of rigidity of the fibre increased with the temperature, at first as a linear function of it, but as the temperature rose the rate of increase gradually diminished, and a maximum rigidity was attained at about 880° C. After passing this point the rigidity decreased very rapidly with increase of temperature.

The internal viscosity of the fibres increased with the temperature at a rate which was at first small and constant, but after about 650° C. it became much more rapid. At 1060° C. the internal friction of the fibres was so great that the torsional vibrations were nearly dead-beat.

"On the Influence of the Time Factor on the Correlation between the Barometric Heights at Stations more than 1000 Miles apart." By F. E. CAVE-BROWNE-CAVE, Girton College, Cambridge. Communicated by Professor KARL PEARSON, F.R.S. Received June 3, and in revised form, December 20, 1904,—Read June 16, 1904.

1. An investigation of the relationship of the daily barometric heights on both sides of the Atlantic Ocean has been in progress for some years, and in a preliminary note by Professor Pearson and myself* some account was given of the contemporaneous relationship of a chain of stations from the extreme north of Norway down the west coasts of Europe and Africa. Observations for this east side of the Atlantic have now been copied for twenty years, as far as stations are available from Norway to the Cape, and the only need here is more aid in the very laborious reductions necessary before any inferences can be drawn. A similar chain of stations from Nova Scotia to the Falkland Isles has been completed, with the exception of Brazil, from which, so far, we have been able to obtain no data whatever.

2. It seemed desirable, before entering on the cross Atlantic correlations, to obtain a better conception of how the time factor influences the intensity of correlation. For this purpose two stations, Wilmington and Halifax, seemed specially appropriate. They are both on the East Atlantic coast, the one in North Carolina and the other in Nova Scotia. The results obtained for these stations afford an illustration of the manner in which the theory of correlation can be used for the purposes of meteorological prediction. In a paper published in 1898,† Professor Pearson and Dr. Lee indicated that the proper way to deal with the pressure relationship between two or more stations was to proceed by the method of correlation; and they illustrated this by the simultaneous correlations of various stations in the British Isles. The corresponding simultaneous correlations for stations from Norway to Sierra Leone were given by Professor Pearson and myself in the note already referred to. The object of the present paper is to illustrate this method of correlation as applied to prediction, the fundamental points being (*a*) the choice of two stations which, although far apart, have a considerable correlation with at least 12, and if possible, 24 hours' interval; (*b*) the determination for any two stations of the interval for which the correlation is a maximum. If the practical meteorologist is accustomed to predict roughly the barometric condition at a station A, from stations B, C, and D, then, if he has observations for twenty years or more for these stations, modern statistical methods place him in a position to choose

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* 'Roy. Soc. Proc.,' vol. 70, pp. 465—470.

† 'Phil. Trans.,' A, vol. 190, pp. 423—469.

the best intervals between the readings in order to find, from the anterior observations at the four stations, the most probable barometric height at A on a given day, and the most probable error of this estimate. They thus supply a means of giving to his predictions a greater precision than is at present attainable. It should also be remembered that, although the present paper only deals with barometric observations, the same methods could be applied to temperature, or to any other of the quantities with which meteorology is concerned.

In order to show that the relations between the two stations mainly considered in this paper are not due to purely local conditions, corresponding investigations have been made for two stations in the Southern Hemisphere, St. Helena and Cape Town. Although the shortness of the period (1893–98) for which observations taken at St. Helena are available, prevents these results from being as fully reliable as those obtained for the North American stations, yet they are sufficient to show the general nature of the pressure relationship between the two places, and the influence of the time factor.

The latitudes and longitudes, and hours of observation are as follows :—*

Halifax, 44° 35′ N., 63° 40′ W.; 9 A.M.

Wilmington, 33° 14′ N., 77° 59′ W.; 7 A.M. up to June 30, 1888, afterwards 8 A.M.

Cape Town, 34° 0′ S., 18° 35′ E.; 8 A.M.

St. Helena, 15° 57′ S., 5° 40′ W.; 9 A.M.

This gives an arc of about 15° 51′, or about 1090 miles between Halifax and Wilmington, and 28° 18′, or about 1950 miles between Cape Town and St. Helena. Roughly speaking, Halifax is north-east of Wilmington, and Cape Town south-east of St. Helena.

The twenty years of the data for Halifax and Wilmington were divided into two decades, 1879–88 and 1889–98, and the summer and winter months (equinox to equinox) were dealt with separately. As was pointed out in the previous note, there is a marked difference between the summer and winter results, and two ten-year periods were desirable for mutual control. It soon became obvious that the summer and winter time factors were different in character, the interval for maximum correlation being considerably shorter in the summer. The numbers obtained indicate that change of pressure passes from Wilmington to Halifax, *i.e.*, from south-west to north-east, and thus it is desirable to take Wilmington earlier in order to predict for Halifax later. For the southern pair of stations there is the same kind of difference between the summer and winter results; this seems to indicate that the phenomenon is really connected with the season, and does not depend on influences external to the Earth, since the summer for the first pair is the winter for the second. Moreover, it is found that for the two southern stations the change of pressure passes from north-west to south-east, so that in predicting we ought to take St. Helena earlier than Cape Town. The following tables give the correlations obtained:—

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* The Canadian Meteorological Office kindly superintended the copying of the Halifax and other Canadian data, the cost of which was defrayed by Professor Pearson; the Smithsonian Institution provided the copies of the Wilmington and other United States data; the readings for Cape Town we owe to the mediation of Dr. W. N. Shaw, who procured them from the Cape Meteorological Committee, the cost of copying them being defrayed by a grant from the Government Grant Committee of the Royal Society.

Table I.—Correlation of Barometric Heights at Halifax and Wilmington.

Interval between readings.*	Summer, 1879—1888.	Winter, 1879—1888.	Interval between readings.	Summer, 1889—1898.	Winter, 1889—1898.
hrs.			hrs.		
−118	+0·0585	—	−119	−0·0134	—
− 94	+0·0605	—	− 95	−0·0247	—
− 70	+0·0668	+0·0496	− 71	−0·0141	+0·0512
− 46	+0·1391	+0·0379	− 47	+0·0418	+0·0598
− 22	+0·2385	+0·0416	− 23	+0·1742	+0·0420
+ 2	+0·3432	+0·2878	+ 1	+0·3038	+0·2456
+ 26	+0·3714	+0·5206	+ 25	+0·3143	+0·4701
+ 50	+0·2176	+0·2344	+ 49	+0·1538	+0·2263
+ 74	+0·1138	+0·0842	+ 73	+0·0581	+0·0839
+ 98	+0·0816	+0·0342	+ 97	+0·0150	+0·0736
+122	+0·0881	+0·0217	+121	−0·0050	+0·0881

Table II.—Correlation of Barometric Heights at Cape Town and St. Helena.

Interval between readings.†	Summer, 1893—1898.	Winter, 1893—1898.
hrs.		
−97	+0·2202	+0·2898
−73	+0·2278	+0·2470
−49	+0·2620	+0·2405
−25	+0·3461	+0·2919
− 1	+0·4478	+0·3927
+23	+0·4468	+0·4605
+47	+0·3434	+0·4081
+71	+0·2908	+0·3409
+95	+0·3083	+0·3130
+119	+0·2950	+0·2785

* **Positive when the reading is taken later at Halifax.**

† **Positive when the reading is taken later at Cape Town.**

3. It seemed desirable to determine the intervals for which the correlation between each pair of stations is greatest, and also the values of these maxima. After some consideration, the curve

$$\log y = a_0 + a_1x + a_2x^2 + a_3x^3 + a_4x^4$$

was selected as likely to give a reasonable interpolation result,* the axis of y being that of the correlation, and x being the interval, in days, between the readings, counted as positive when the observation is taken later at the more easterly station in each case. The curves are not intended to represent the complete correlation data, but they have been used as convenient empirical methods to find in position and magnitude the maximum ordinates. For this reason only five correlations were used for calculating each curve, namely, those given in rows 5 to 9 of Table I, and rows 4 to 8 of Table II. The following curves were determined :—

WILMINGTON AND HALIFAX.

Summer, 1879—1888 :—

$$\log_{10} y = -0\cdot477451 + 0\cdot161608x - 0\cdot062808x^2 - 0\cdot058772x^3 + 0\cdot014994x^4.$$

Maximum ordinate : 0·3877 at $x = 0\cdot7275$, *i.e.*, 17·46 hours.

Summer, 1889—1898 :—

$$\log_{10} y = -0\cdot524516 + 0\cdot175661x - 0\cdot122239x^2 - 0\cdot040868x^3 + 0\cdot012096x^4.$$

Maximum ordinate : 0·3386 at $x = 0\cdot5862$, *i.e.*, 14·07 hours.

Winter, 1879—1888 :—

$$\log_{10} y = -0\cdot592740 + 0\cdot647374x - 0\cdot300470x^2 - \cdot054822x^3 + 0\cdot021968x^4.$$

Maximum ordinate : 0·5272 at $x = 0\cdot9553$, *i.e.*, 22·92 hours.

Winter, 1889—1898 :—

$$\log_{10} y = -0\cdot634964 + 0\cdot615514x - 0\cdot258629x^2 - 0\cdot073287x^3 + 0\cdot025021x^4.$$

Maximum ordinate : 0·4721 at $x = 0\cdot9674$, *i.e.*, 23·22 hours.

ST. HELENA AND CAPE TOWN.

Summer, 1893—1898 :—

$$\log_{10} y = -0\cdot346171 + 0\cdot063222x - 0\cdot064491x^2 - 0\cdot011993x^3 + 0\cdot006497x^4.$$

Maximum ordinate : 0·4660 at $x = 0\cdot4518$, *i.e.*, 10·84 hours.

Winter, 1893—1898 :—

$$\log_{10} y = -0\cdot400900 + 0\cdot119333x - 0\cdot039277x^2 - 0\cdot022393x^3 + 0\cdot006580x^4.$$

Maximum ordinate : 0·4596 at $x = 0\cdot9994$, *i.e.*, 23·986 hours.

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* The suggestion is due to Mr. W. Palin Elderton.

4. It therefore appears that the maximum correlation between Halifax and Wilmington in the summer occurs when the barometer at Halifax is read about 16 hours later than that at Wilmington, and that the corresponding interval for the winter is about 23 hours. The intervals for St. Helena and Cape Town are about 11 hours and 24 hours respectively. Some caution may be necessary in accepting the values obtained for the summer intervals, since it is possible that the diurnal variation may affect the correlation; this point could only be settled by means of observations taken at other hours of the day. This effect of the diurnal variation, if it really exists, may conceivably account for some part of the difference between the intervals obtained for the summer months of the two decades for the American stations. Nevertheless, it seems reasonable to conclude that, in order to predict the barometric height at Halifax at 9 A.M., it is desirable to use the reading taken at Wilmington at 10 A.M. on the previous morning in the winter, while in the summer the Wilmington reading should be taken at about 5 P.M.

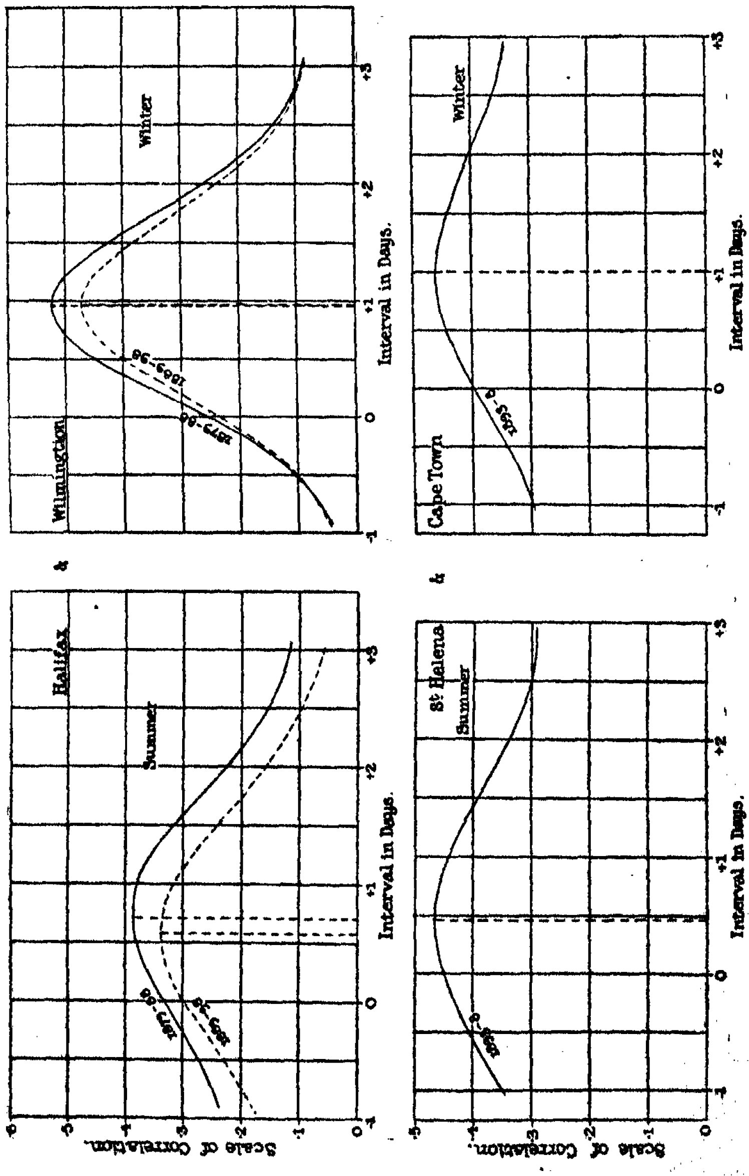
Diagram I (next page) shows the interpolation curves used.

5. The physical interpretation of these intervals for which the correlation is a maximum, is not obvious to me, although it may possibly be so to practical meteorologists. Of course, the intervals, 11 to 24 hours, are too short to be looked upon as corresponding to the transfer of an actual disturbance between the stations. Even if this were not the case, they could not give the average intervals between the arrival of the same isobar at the two places considered, since none of the pressures correlated may be alike. I should be glad to see the point adequately treated by one with practical meteorological experience, and will merely remark here that the correlation depends not upon equality of pressure, but upon proportionality of deviations from the local means. A full explanation must also account for the fact that the winter and summer relations differ in a very marked way.

6. Another point which seemed to deserve investigation was the correlation between the daily rise or fall of the barometer at Halifax and Wilmington. This investigation would have involved considerable labour if it had been necessary to proceed by the direct method of preparing tables of the daily rise or fall, and then calculating the correlations from them. The work has been considerably lessened by the use of the following method, which is due to Professor Pearson.

Let x_1 be the reading on one day and x_2 that on the following day at the first station, x_1' and x_2' the corresponding readings at the second station after any interval. Let m_1, m_2, m_1', m_2' be the means, σ_1, σ_2, σ_1', σ_2' the standard deviations, r_{12} the correlation of x_1 and x_2, $r_{1'2'}$, that of x_1' and x_2', $r_{12'}$, that of x_1 and x_2', and so on, and R that of $(x_1 - x_2)$ and $(x_1' - x_2')$. The mean values of $(x_1 - x_2)$ and $(x_1 - x_2')$ will

DIAGRAM I.



clearly be $m_1 - m_2$ and $m_1' - m_2'$ respectively. Hence, if N be the number of pairs correlated, and if S denotes summation, we have

$$R = \frac{S\{(x_1 - x_2) - (m_1 - m_2)\}\ \{(x_1' - x_2') - (m_1' - m_2')\}}{N\sqrt{S\{(x_1 - x_2) - (m_1 - m_2)\}^2}\sqrt{S\{(x_1' - x_2') - (m_1' - m_2')\}^2}}$$

$$= \frac{\sigma_1\sigma_1' r_{11'} - \sigma_2\sigma_1' r_{21'} - \sigma_1\sigma_2' r_{12'} + \sigma_2\sigma_2' r_{22'},}{\sqrt{(\sigma_1^2 + \sigma_2^2 - 2\sigma_1\sigma_2 r_{12})(\sigma_1'^2 + \sigma_2'^2 - 2\sigma_1'\sigma_2' r_{1'2'})}} \quad \dots\dots\dots\dots$$

It may be noted that this formula would apply to any case in which it was desired to correlate the difference of one pair of quantities with the difference of another pair. If we were not dealing with the summer and winter months separately, we should have, with sufficient approximation,

$$\sigma_1 = \sigma_2, \qquad \sigma_1' = \sigma_2', \qquad r_{11'} = r_{22'},$$

since the quantities included in the x_1 and the x_2 groups would be the same, with the exception of a single reading at each end of the period considered. The formula would then take the simple form

$$R = \frac{2r_{11'} - r_{21'} - r_{12'}}{2\sqrt{(1 - r_{12})(1 - r_{1'2'})}} \quad \dots\dots\dots\dots\dots\dots\dots \quad \text{(ii)}.$$

But in our case the x_1 and x_2 groups differ by a reading at each equinox of each year considered, and it was therefore decided to use the accurate equation (i), although (ii) would have been sufficient to give a good idea of the correlation.

In order to use this formula, it was necessary to calculate the correlations between the barometric heights on consecutive days at Halifax and at Wilmington. Table III gives these correlations, and Table IV gives the correlations between the daily rise at the two stations for various intervals.

Table III.—Correlation of Barometric Heights on Consecutive Days.

Station.	Summer, 1879—1888.	Winter, 1879—1888.	Summer, 1889—1898.	Winter, 1889—1898.
Halifax	0·5924	0·3998	0·5155	0·4270
Wilmington	0·6151	0·4827	0·6510	0·4916

The most noticeable fact which appears from these results is the analogy between them and the space relations considered in the previous note. In that case we found that with increasing distance the correlation diminished to a negative minimum, and then began to increase; and the negative correlations obtained were of considerable magnitude. This does not seem to occur for the time relations when the actual readings are considered; for, although the values given in Tables I and II seem to indicate that a minimum has been reached, the only negative correlations which have been found are so small as to be

Table IV.—Correlation of Daily Rise at Halifax and Wilmington.

Interval between readings.*	Summer, 1879—1888.	Winter, 1879—1888.	Interval between readings.	Summer, 1889—1898.	Winter, 1889—1898.
hrs.			hrs.		
−94	−0·0071	—	−95	−0·0849	—
−70	−0·0801	—	−71	−0·0540	—
−46	−0·0298	−0·0166	−47	−0·0899	+0·0241
−22	−0·0107	−0·2152	−23	+0·0034	−0·2047
+ 2	+0·0960	+0·0183	+ 1	+0·1450	−0·0200
+26	+0·2268	+0·4676	+25	+0·2043	+0·4368
+50	−0·0669	−0·1205	+49	−0·0775	−0·0950
+74	−0·0919	−0·0901	+73	−0·0638	−0·1227
+98	−0·0391	−0·0367	+97	−0·0199	−0·0260

of very little significance. But it does occur in a very marked way for the time relations when we correlate the daily rise at the two stations. This analogy strengthens our belief that the intervals of maximum correlation are of great importance from the standpoint of atmospherical physics, and our desire to see the practical meteorologist's explanation of the matter is correspondingly increased.

7. The magnitude of the correlations which have been found to exist between the readings on consecutive days at Wilmington and Halifax, suggests the possibility of predicting barometric heights at the latter station with a fair degree of accuracy from the heights observed at Wilmington on the previous day. In the paper by Professor Pearson and Dr. Lee already referred to, a table is given showing the barometric heights at Stonyhurst on 50 days, calculated from the simultaneous readings at Southampton and Laudale. The difference between the calculated and observed heights at Stonyhurst was small in every case, the mean value being about $\frac{1}{10}''$. At that time no correlations had been calculated between observations taken on different days; but the values now obtained make it possible to apply the theory to actual prediction. In predicting for Halifax from a single station more than 1000 miles away, we are naturally unable to obtain such good results, but, on the other hand, we have the advantage of calculating the probable heights at Halifax a day beforehand. In order to see how far the prediction is verified, forty dates were taken at random, one in summer, and one in winter for each year. It was impossible to allow the best intervals, 16 hours in summer, and 23 in winter, as we do not possess readings for Wilmington taken at the required times, and the predictions have, therefore, been made with the interval of 26 hours for the first 10 years, and 25 for the second.

* Positive when the readings are taken later at Halifax.

Table V gives the means, standard deviations, and regression coefficients which were employed in the calculations.

Table V.—Barometric Constants for Halifax and Wilmington.

Station and season.	Mean.	Standard deviation.	Regression.
Halifax, summer, 1879—1888	29″·842	0″·2446	0·6096
Wilmington, do.	30·045	0·1490	
Halifax, summer, 1889—1898	29·870	0·2215	0·4681
Wilmington, do.	30·085	0·1487	
Halifax, winter, 1879—1888	29·882	0·3446	0·8764
Wilmington, do.	30·152	0·2047	
Halifax, winter, 1889—1898	29·868	0·3436	0·7678
Wilmington, do.	30·158	0·2104	

The corresponding prediction equations are as follows, if H_p denote the probable height at Halifax corresponding to a height W observed at Wilmington on the previous day.

Summer 1879—1888 .... $H_p = 11{\cdot}527 + 0{\cdot}6096W$.
Summer 1889—1898 .... $H_p = 15{\cdot}787 + 0{\cdot}4681W$.
Winter 1879—1888............ $H_p = 3{\cdot}457 + 0{\cdot}8764W$.
Winter 1889—1898............ $H_p = 6{\cdot}713 + 0{\cdot}7678W$.

These results bring out clearly the marked difference between summer and winter, which has already been shown in the case of the correlations. But in both cases there is also a difference between the two decades reduced; this is partly due, no doubt, to the fact that the Wilmington observations were taken at different hours in the two decades, but this would not account for the whole difference, which has been found also in dealing with other stations. It may be due to variations corresponding to those of random sampling; or it may indicate a gradual change, whether periodic or progressive, in the physical constants involved; and this question can only be settled by dealing with observations extending over a longer period.

The results of the predictions are shown in Table VI.

The theoretical mean error $= 0{\cdot}7979\sigma\sqrt{1-r^2}$

$= 0{\cdot}175$ for summer and $0{\cdot}239$ for winter,

taking the mean summer and mean winter values of σ and r for the two decades. These theoretical errors are slightly larger than the actual mean errors for the forty random dates here considered. We should presumably improve the predictions by taking the interval for which the correlation is a maximum; but even without this improvement the degree of accuracy attained, though not very great, might be

Table VI.—Comparison of Predicted and Observed Heights at Halifax.

A. *Summer Months.*

Date.	Predicted height.	Observed difference.	Date.	Predicted height.	Observed difference.
June 30, 1879 ..	29·738	−0·152	May 8, 1889....	29·844	+0·017
Aug. 17, 1880 ..	29·930	+0·264	April 20, 1890 ..	29·848	+0·245
April 11, 1881 ..	29·789	−0·030	July 1, 1891....	29·771	+0·120
July 4, 1882 ...	29·782	+0·117	Aug. 12, 1892 ..	29·876	−0·061
Sept. 16, 1883 ..	29·922	+0·035	Sept. 7, 1893 ...	29·881	+0·089
April 30, 1884 ..	29·868	−0·306	June 9, 1894 ...	29·902	+0·021
June 14, 1885 ..	29·891	−0·033	July 8, 1895....	29·782	−0·064
March 31, 1886	29·853	+0·235	April 26, 1896 ..	29·842	+0·386
May 16, 1887...	29·991	+0·153	May 13, 1897...	29·875	+0·036
July 20, 1888...	29·924	+0·152	June 17, 1898 ..	29·897	−0·117
Mean error ..	..	0·148	Mean error..	..	0·111

B. *Winter Months.*

Date.	Predicted height.	Observed difference.	Date.	Predicted height.	Observed difference.
Dec. 25, 1879 ...	30·016	−0·396	Nov. 16, 1889...	29·922	+0·194
Oct. 1, 1880	29·905	+0·190	Jan. 5, 1890....	30·126	+0·128
Nov. 25, 1881...	29·502	+0·068	Oct. 28, 1891...	29·688	+0·069
Feb. 21, 1882...	29·951	+0·158	Feb. 14, 1892...	29·888	−0·240
Jan. 11, 1883 ...	29·593	+0·053	Dec. 2, 1893....	29·766	−0·240
Sept. 30, 1884 ..	29·824	+0·102	Jan. 28, 1894...	29·924	+0·146
March 7, 1885 ..	29·894	+0·117	Oct. 1, 1895	29·718	+0·004
Feb. 1, 1886	29·646	+0·199	Dec. 10, 1896...	29·730	−0·425
Dec. 9, 1887	29·898	+0·305	Feb. 25, 1897...	29·958	+0·211
Nov. 2, 1888	30·108	−0·004	Nov. 9, 1898 ...	30·114	+0·029
Mean error ..	..	0·168	Mean error..	..	0·169

sufficient to be of service in practical meteorology. Still better results could probably be obtained by making the prediction for one station depend upon observations at two or more other stations, so situated as to give suitable intervals for maximum correlation*; and it may also be desirable to take into account the height observed on the previous day at the station for which the prediction is required, for the results given in Table III show that in some cases, at any rate, there is a considerable correlation between the barometric readings on successive days at the same station. Moreover, it is possible that the correlation between the daily rise or fall at different stations might give better results for prediction than the correlation between the actual heights observed; but what has already been done is sufficient to indicate the manner in which modern statistical methods may aid the meteorologist in this part of his work. As regards the more fundamental, though less immediately useful, task of meteorological science, the intervals of maximum correlation, a few examples of which have been considered in this paper, will, I believe, be found ultimately to be of importance in relation to the physics of the atmosphere. Although considerable labour is involved in the calculation of these intervals, even for a single pair of stations, yet the increase of theoretical knowledge which would result from an adequate investigation of the manner in which they depend upon local conditions, and upon the positions and distances of the places considered, would probably be amply sufficient to justify the labour expended upon the matter.

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* It would be of little use to predict for intervals of only 5 or 6 hours; at least 24 hours would be desirable, if this does not make it necessary to take distances so great as seriously to weaken the correlation.

8. The conclusions to be drawn from the results given in this paper are as follows:—

(i) The correlation between the barometric readings at two stations upwards of 1000 miles apart depends upon the interval between the readings. In the case of Halifax and Wilmington, the correlation is sensible for at least 9 days, and it reaches a maximum for an interval of about 16 hours in summer and 23 in winter. For these stations, and also for St. Helena and Cape Town, the observation at the more easterly station should be taken later for maximum correlation.

(ii) There is a considerable correlation between the daily rise at Halifax and Wilmington, and this correlation changes with the interval in a manner somewhat analogous to that in which the correlation between simultaneous heights at two stations approximately on the same meridian depends upon the distance between them.

(iii) There are considerable differences between the summer and winter correlations, and these differences are of the same general nature for both pairs of stations considered.

(iv) It is possible to predict the barometric height at one station from an earlier height at a second station more than 1000 miles away, with a fair degree of accuracy, the mean observed error for forty dates, taken at random, for Halifax and Wilmington, being 0″·15.

"On the Drift produced in Ions by Electromagnetic Disturbances, and a Theory of Radio-activity." By George W. Walker, M.A., A.R.C.Sc., Fellow of Trinity College, Cambridge, Lecturer on Physics in the University of Glasgow. Communicated by Professor A. Gray, F.R.S. Received December 16, 1904,—Read January 26, 1905.

Some time ago I showed* how the equations of motion of a free ion under the influence of a harmonic train of plane waves might be completely integrated, subject to the restriction that the viscous effect of radiation from the ion may be neglected.

The equations are closely analogous to those for a simple pendulum, and by following out the analogy in the case where the pendulum makes complete revolutions, it is easy to show that while the passage of a complete wave restores the initial velocities of the ion, its position in space is altered. This change of position cannot be accounted for entirely by the change due to velocity which the ion may be assumed to possess before the wave reaches it.

The continuance of the waves thus involves the result that the ion must continue to change its position in space. It will thus appear to move in a definite manner which can be determined in terms of the initial circumstances of the ion and the constants of the train of waves. The result is very remarkable, and is not confined to an infinite train of harmonic waves. Similar results follow in the case of any form of electro-magnetic disturbance propagated in a straight line.

I propose here to discuss the case of a plane polarised disturbance propagated in a straight line. Let the electric force be $X = X_0 f(Vt - z)$ where V is the velocity and z the direction of propagation. Associated with this we must have a magnetic force $M = X_0/V \; f(Vt - z)$ in a direction at right angles to that of X. If m be the inertia and e the charge of the ion, the equations of motion may be written

$$m\ddot{x} = e(X - \dot{z}M),$$

$$m\ddot{y} = 0,$$

$$m\ddot{z} = +e\dot{x}M.$$

We may thus confine attention to the motion in the xz plane. We have

$$\ddot{x} = \frac{e}{m}\frac{X_0}{V}(V - \dot{z})f(Vt - z),$$

$$\dot{z} = \frac{e}{m}\frac{X_0}{V} x f(Vt - z).$$

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* 'Roy. Soc. Proc.,' vol. 69, p. 394; 'Phil. Mag.,' 1903, vol. 6, p. 537.

If we take a moving origin so that $Vt-z=\zeta$, then ζ will be the distance of the ion from a plane moving with the disturbance, and reckoned positive in the direction from which the waves come. The equations then take the form

$$\ddot{x} = \frac{e}{m}\frac{X_0}{V}\dot{\zeta}f(\zeta),$$

$$\ddot{\zeta} = -\frac{e}{m}\frac{X_0}{V}\dot{x}f(\zeta).$$

Thus in general

$$\dot{x}^2+\dot{\zeta}^2 = \text{const.}$$

is an integral; it indicates that the energy of the ion relative to the moving origin is constant.

We also get

$$\dot{x} = a+\frac{e}{m}\frac{X_0}{V}\int_0^{\zeta} f(\zeta)\,d\zeta,$$

where a is a constant,

We may note that if the disturbance is such that

$$\int_0^{\zeta_1} f(\zeta)\,d\zeta = 0,$$

then the original value of $\dot{x}$ is restored, when $\zeta=\zeta_1$, and hence also the original values of $\dot{\zeta}$ or $\dot{z}$ on account of the equation of energy.

Let us now take a simple case so that

$$\begin{array}{llll} f(\zeta) = 1 & \text{from} & 0 & \text{to } d, \\ f(\zeta) = 0 & \quad ,, & d & \,,,\ d+l, \\ f(\zeta) = -1 & \quad ,, & d+l & \,,,\ 2d+l, \\ f(\zeta) = 0 & \quad ,, & 2d+l & \,,,\ 2d+2l, \end{array}$$

and thereafter let the form of disturbance recur.

From $\zeta=0$ to $\zeta=d$, we have

$$\ddot{x} = \frac{eX_0}{mV}\dot{\zeta}, \qquad \ddot{\zeta} = -\frac{eX_0}{mV}\dot{x}.$$

Hence

$$\dot{x} = a+\frac{eX_0}{mV}\zeta, \qquad \dot{\zeta} = c-\frac{eX_0}{mV}x;$$

and

$$\dot{x}^2+\dot{\zeta}^2 = a^2+c^2,$$

where a and c are the initial values of $\dot{x}$ and $\dot{\zeta}$.

We also get

$$\left(a+\frac{eX_0}{mV}\zeta\right)^2+\left(c-\frac{eX_0}{mV}x\right)^2 = c^2+a^2.$$

Thus during the first pulse the ion describes a circle centre

$\left(\frac{mV}{eX_0}c, \; -\frac{mV}{eX_0}a\right)$ and radius $\frac{mV}{eX_0}(a^2+c^2)^{\frac{1}{2}}$, with angular velocity $\frac{eX_0}{mV}$. It will leave the first pulse with velocity given by

$$\dot{x} = a + \frac{eX_0}{mV}d, \qquad \dot{\zeta} = \left\{c^2+a^2-\left(a+\frac{eX_0}{mV}d\right)^2\right\}^{\frac{1}{2}},$$

and describe a straight line until it reaches the second pulse.

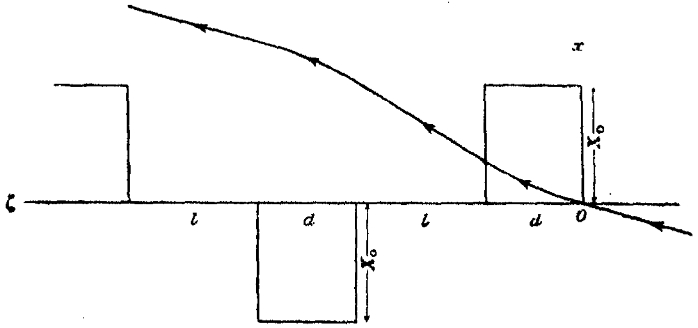
During the passage through the second pulse we have

$$\ddot{x} = -\frac{eX_0}{mV}\dot{\zeta}, \qquad \ddot{\zeta} = +\frac{eX_0}{mV}\dot{x};$$

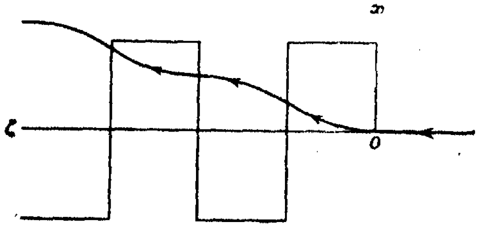
so that

$$\dot{x}^2+\dot{\zeta}^2 = a^2+c^2.$$

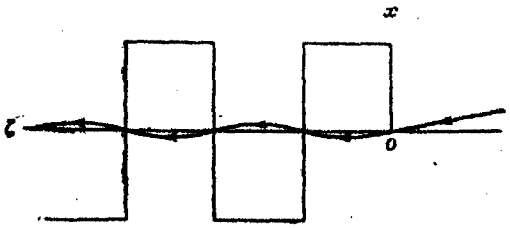
Fig. 1.—Diagram to illustrate the path of the ion.



Figs. 2 and 3.—Diagrams to illustrate the path of the ion when $l = 0$.



Case I. $a = 0$. $c = V$.



Case II. $a = -\frac{1}{2}\omega d$. $c = V$.

Thus the ion will describe a circle of the same radius as before with the same angular velocity, but the curvature is now in the opposite direction and the centre is different. The ion leaves the second pulse with velocity (a, c), and proceeds in a straight line. The path is shown in the diagram (1).

We now calculate the time taken to travel from $\zeta = 0$ to $\zeta = 2l + 2d$, and also the displacement. The simple character of the path enables us to do this easily.

If we denote eX_0/mV by ω, the time, T, is given by

$$T = \frac{2}{\omega}\left\{\sin^{-1}\frac{a+\omega d}{(c^2+a^2)^{\frac{1}{2}}} - \sin^{-1}\frac{a}{(c^2+a^2)^{\frac{1}{2}}}\right\}$$

$$+\frac{l}{c}+\frac{l}{\{c^2+a^2-(a+\omega d)^2\}^{\frac{1}{2}}}.$$

Now, $\zeta = Vt - z$. Hence the displacement of the ion from its original position, in the direction of the waves, is

$$z = VT - 2(l+d).$$

The displacement in the direction of x is

$$x = \frac{2}{\omega}\{c - \sqrt{c^2+a^2-(a+\omega d)^2}\}$$

$$+\frac{al}{c}+\frac{(a+\omega d)\,l}{\sqrt{c^2+a^2-(a+\omega d)^2}}.$$

Let us now consider two particular cases.

Case I.—The ion was originally at rest. Hence $a = 0$ and $c = V$. Neglecting ω^4 and higher terms, we get

$$T = 2\frac{d+l}{V}+\frac{\omega^2 d^2}{V^3}\left(\tfrac{1}{3}d+\tfrac{1}{2}l\right).$$

$$z = \frac{\omega^2 d^2}{V^2}\left(\tfrac{1}{3}d+\tfrac{1}{2}l\right).$$

$$x = \frac{\omega d}{V}(d+l)+\frac{\omega^3 d^3}{V^3}\left(\tfrac{1}{4}d+\tfrac{1}{2}l\right).$$

Thus, if the impulses recur, the ion will appear to travel in space with velocities which are approximately

$$\dot{x} = \tfrac{1}{2}\,\omega d \quad \text{and} \quad \dot{z} = \frac{\omega^2 d^2}{V}\,\frac{(d+\frac{3}{2}\,l)}{6\,(d+l)}.$$

It will thus appear to drift on in the direction of the waves.*

---

* These are also the mean values of the true velocities $\dot{x}$ and $\dot{z}$ during a complete pulse. I wish to emphasize the fact that if we could observe the ion just as it leaves the pulse it will again be at rest if it was initially at rest, but its position is altered. I shall therefore refer to these as apparent velocities.

Case II.—Let $\dot{x} = -\frac{1}{2}\omega d$ and $\dot{z} = 0$ initially.

Thence $a = -\frac{1}{2}\omega d$ and $c = \mathrm{V}$.

In this case

$$\mathrm{T} = 2\frac{d+l}{\mathrm{V}} - \frac{\omega^2 d^2}{\mathrm{V}^3}\,\tfrac{1}{6}d, \text{ q.p.}$$

$$z = -\frac{\omega^2 d^2}{\mathrm{V}^2}\,\tfrac{1}{6}d, \text{ q.p.}$$

$$x = 0 \text{ exactly.}$$

Thus the apparent velocities are

$$\dot{x} = 0 \text{ exactly,}$$

$$\dot{z} = -\tfrac{1}{12}\frac{\omega^2 d^2}{\mathrm{V}}\frac{d}{d+l}.$$

Thus the ion will seem to move in the direction from which the impulses come. It is worth while to note that the x velocity vanishes, and so the ion will drift backwards without altering its x co-ordinate.

In both these cases the initial circumstances are such that the ion succeeds in getting through the first pulse. It will be seen that the initial circumstances can be so chosen that it fails to do so. This, however, involves the result that at some point of the circular path $\zeta = 0$, or in other words that the ion is moving with the velocity of the waves. Now the equations break down before this point; but the result may be held to indicate that if the ion is originally moving in the direction z with a velocity a little less than V, it may, so to speak, be picked up by the waves and carried forward with the velocity V.

These cases are sufficient to illustrate the general feature, and it may be noted that the apparent x velocity is an odd function of the charge e, while the z velocity is an even function of the charge. This last result leads us to expect that even a neutral molecule made up of positive and negative ions will also be made to drift in the direction in which the waves are travelling.

We thus arrive at the conclusion that the propagation of plane polarised disturbances through a portion of space containing ions involves drifting of both positive and negative ions which may be with or against the direction of propagation according to the initial circumstances. Since the z motion does not depend on the orientation of the plane of polarisation, similar results must follow for unpolarised disturbances.

The restoration of the initial velocities relative to the fixed origin, after the passage of what we may call a complete pulse, shows that no energy (relative to the fixed origin) is permanently abstracted by the ions, although during one portion of the pulse energy is abstracted which is exactly restored during the remaining portion. If, however, we take account of radiation from the ion, this will no longer be the case. Energy will be definitely abstracted from the pulses and radiated away from the ion. In this case the passage of a complete pulse no longer restores the original velocities unless the energy absorbed by the ions is radiated away before the pulse has passed. This will not, in general, be the case. Hence, even if radiation be taken into account, there must still be a drifting of the ions. Indeed, the general effect of the radiation will be to give the ions real velocities instead of what I have called apparent velocities.

These results seem to me to have an important bearing on the theory of Röntgen rays and of the action of radio-active substances. We may regard a radio-active substance as the origin of electro-magnetic disturbances radiated outwards. These may ionise the gas in the immediate vicinity of the substance, and we shall then have a streaming of positive and negative ions and probably also of neutral molecules, both outwards from the substance and inwards to it. This view is quite in agreement with the apparently material character of part of the radiations (indeed it would explain it), but it does not require the supposition that there is a continual diminution of the radio-active substance.

The question arises whether the velocities set up in the ions are of the order that experiment indicates. If the impulses radiated are set up by collisions of ions in the active substance, it appears to me that at least in the immediate vicinity of the substance, the velocities set up may be comparable with the velocities of the ions which produced the impulses.

The velocity of the material particles in the radiations from active substances are comparable with V. It will thus be seen that the theory suggested here requires that ωd should be comparable with V. Now ω is the angular velocity with which the ion described the circular path in passing through the pulse, and is thus the measure of the frequency of the vibrations set up in the ion. If d is of the order of a wave length of visible or ultra-violet light, then ω must be of the order of the frequency of visible or ultra-violet vibrations. Hence the theory requires that associated with the impulses we should have visible or ultra-violet light. I think it must be admitted that this is in harmony with the experimental evidence on ionising agents generally. Per contra we may argue that if any system is an origin from which electro-magnetic pulses of great intensity are radiated, we shall have associated with these, in its immediate vicinity, streams of ions moving with great velocities, and trains of waves which may be of such frequency as to come within the visible spectrum. Thus the distinction between bodies turns on the character of the impulses, and is a difference of degree rather than of kind.

Another interesting point is raised by these results. In free space the propagation of waves in a straight line is quite independent of any statical electric or magnetic field. But if the waves are propagated through a part of space containing matter, the streaming of the ions produced by the waves seems to lead to the conclusion that the propagation of the waves is no longer independent of the statical electric and magnetic field, and aberration must result.

In conclusion, I wish to express my great obligation to Professor Gray, who has discussed these results with me and read the paper with very great care.

[*Note added January* 30.—Lord Kelvin has expressed the view that a radio-active body may in some way extract energy from the æther and again radiate it. Professor and Madame Curie have also suggested a possible abstraction from the surrounding gas. The results obtained here support such views and indicate in some measure how such a process of selection may go on.]

"On the Ultra-Violet Spectrum of Gadolinium."* By Sir WILLIAM CROOKES, D.Sc., F.R.S. Received December 8,—Read December 15, 1904.

Gadolinium oxide is a rare earth, occurring between yttrium and samarium. It was discovered in 1880 by Marignac, and was at first called by him Yα, a designation which he soon changed for gadolinium. Since Marignac's time much work has been done on this earth by Lecoq de Boisbaudran, Bettendorf, Cleve, Benedicks, Marc, Demarçay, Exner and Haschek, Urbain, and others.

In the spring of this year, M. G. Urbain gave me some gadolinia and other rare earths, which he had prepared in a state of considerable purity by means of a novel system of fractionation in which use is made of the crystallisation of double nitrates of bismuth and magnesium with the rare earth nitrates. He finds that bismuth places itself between the ceric and the terbic groups, thus sharply separating samarium, the last member of the ceric group, from europium and gadolinium, the first members of the terbic groups. I have for some time past been fractionating rare earths by Urbain's method, and can quite corroborate what he says.

The ultra-violet spectrum of gadolinium has been measured by Exner and Haschek, who have published their results in a book,

[* A plate of the spectrum to which this communication refers will, it is hoped, be published in another place.]

"Wellenlängen-Tabellen für Spektralanalytische Untersuchungen,"[*] These observers used a material prepared by Dr. L. Haitinger, in which they say holmium, samarium, and yttrium were present as impurities. They give wave-lengths of 1150 lines; I have found them to be as a rule very accurate, and in the maps accompanying this I have adopted most of their wave-lengths, except in cases where my own measurements give different figures, or where lines given by them are not to be distinguished on my photographs. In some cases also lines ascribed to gadolinium appear to be caused by other earths as impurities.

My photographs were taken by means of the apparatus described in my paper "On the Ultra-Violet Spectrum of Radium."[†] The arrangement is the same as there adopted in the maps of the radium spectrum. The upper half of each strip shows the iron lines used as standards, with their wave-lengths according to Rowland's latest measurements. The lower half contains the gadolinium lines, with their wave-lengths re-calculated or verified from the iron standards, according to the method given in detail in the paper just quoted. Other lines, the wave-lengths of which are written in red ink, are either platinum lines or lines due to traces of impurity in the gadolinium oxide. These are very few, and their faintness speaks well for the accuracy with which M. Urbain has separated other earths from the gadolinium, for in my experience I have seldom found a so-called "pure" salt of an ordinary metal anything like so free from impurities as this earth proves to be. Moreover, it must not be taken as certain that some of the impurities assumed to be present on the strength of a strong line are really there, because in some instances I have not been able to detect the presence of another equally characteristic line of the same impurity.

The rare elements allied to gadolinium, or occurring with it, which I have thus found to be present, are:—

Yttrium,	represented by the lines at...	3774·51 and 4177·68.
Europium	,, ,, ,, ...	3972·16, 4129·90, and 4662·08.
Samarium	,, ,, ,, ...	3230·65.
Ytterbium	,, ,, ,, ...	3289·52 and 3694·35.
Scandium	,, ,, ,, ...	3572·71, 3613·96, and 3630·86.

The other elements which are present are—

Bismuth,	represented by the line at	4259·85.
Magnesium	,, ,, lines at	2796·62 and 2802·80.
Calcium	,, ,, ,, ...	3933·81 and 3968·60.

Of these, the bismuth and magnesium are present from the salts used in the fractionation,* while calcium is represented by the great H and K pair, which are almost always present in earthy spectra.

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[*] F. Deuticke, Leipzig and Wien, 1902.

[†] 'Roy. Soc. Proc.,' vol. 72, p. 295., Aug., 1903.

I have also examined the phosphorescent spectrum of Urbain's gadolinium by means of photography. In 1886 I communicated a paper to the Royal Society,† on the visible spectrum of phosphorescing Yα (gadolinia), given to me by Marignac, and also prepared by myself, and later in the year‡ I said that the gadolinium I was then working with showed, on the evidence of its phosphorescent spectrum, the presence of samarium and other impurities. Since that time I have used the photographic method of examining phosphorescent spectra, and in 1899 I brought before the Royal Society,§ a preliminary notice of a new element, Victorium, the existence of which I was led to infer from its chemical properties, and from some bands in its phosphorescent spectrum. These bands consist of a strong group high up in the ultra-violet spectrum, having wave-lengths of 3117—3120, 3060, 3064, and 3219.

The specimens of gadolinia prepared by myself in 1886, as well as that sent me by Marignac, gave these victorium bands faintly, and the gadolinia given me by M. Urbain also showed the same bands in greater strength than the other lines and bands I have ascribed to samarium and yttrium. Early this month M. Urbain has sent me a specimen of gadolinium which he considers quite pure, and on testing it in the vacuum tube for its phosphorescent spectrum I find the victorium bands photograph stronger than they came out in the other specimen. At the same time I do not think that victorium is gadolinium. All the evidence from chemical and phosphorescent data tends to the conclusion that victorium is only present as an impurity in the gadolinium, and the strength with which it reveals its presence is mainly due to the excessive delicacy of the test.

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* In a still purer specimen from M. Urbain, recently received, these impurities are absent.

† 'Roy. Soc. Proc.,' vol. 40, p. 236, Feb., 1886.

‡ 'Roy. Soc. Proc.,' vol. 40, p. 503, June, 1886.

§ 'Roy. Soc. Proc.,' vol. 65, p. 237, May, 1899.

"On the 'Blaze-currents' of the Gall Bladder of the Frog." By ALICE M. WALLER. Communicated by AUGUSTUS D. WALLER, M.D., F.R.S. Received December 1, 1904,—Read January 26, 1905.

(From the Physiological Research Laboratory of the University of London.)

This investigation is a continuation of Dr. Waller's work on the electrical responses to stimulation exhibited by animal and vegetable living tissues, which responses he has designated "Blaze-currents."*

I have employed the method already described by him at length, in the University Series of Lectures entitled "Signs of Life."†

After examining many tissues and organs from the frog and cat, my attention was directed particularly to the liver of the frog, which one would naturally expect to display signs of activity; not obtaining very large responses from the liver, I tested the gall bladder, and to my surprise, observed large electrical variations which occur regularly and without fail, and may be noticed as long as 24 hours *post mortem ranæ*.

The frog is killed; the liver and gall bladder are taken out and placed on a glass plate; unpolarisable electrodes are applied to the liver or gall bladder. The electrodes are always previously tested, and are made so that they give no response to electrical stimulus.

The liver is found to give antidrome currents except when the electrodes are placed one on the surface and one at the hilum; in this case the responsive current runs from the surface to hilum.

Excitation by Single Break Induction Shocks from Berne Coil.

Liver (March 9).

Strength of excitation.		Response.	
Coil at 5000 +	gave	− 0·0005 volt.	Liver placed between electrodes with under surface upwards
−	„	+ 0·0003 „	
10000 −	„	+ 0·0010 „	
+	„	− 0·0013 „	

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* 'Phil. Trans.,' B, vol. 194, p. 184, December, 1900; 'Roy. Soc. Proc.,' vol. 68, p. 79, January, 1901.

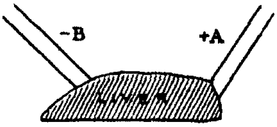
† 'Signs of Life,' published by John Murray, 1903, for the University of London.

Liver (March 24).

Strength of excitation.	**Response.**		**Electrodes.**
5000 −	+0·0010		10000 + = 0·0001
,, +	−0·0009		,, − = 0·0001
10000 +	−0·0013	+0·0002	
−	+0·0022		

Liver.

5000 −	+0·0047		Response surface to hilum
+	+0·0053		
1 hour later—			
10000 +	−0·0047	+0·0002	
−	+0·0047	−0·0003	



Electrodes placed on surface and hilum

Liver (May 7).

5000 + =	−0·0008	+0·0004	
−	+0·0005		
+	−0·0009	+	
10000 +	−0·0018	+0·0004	Remaining and slowly subsiding.
−	+0·0018		

The gall bladder invariably gives an antidrome "blaze" or response to excitation; it is an instance of the equivocal blaze current, in the contrary direction to the exciting current, described by Waller in vol. 68, p. 79, 'Proc. Roy. Soc.' Weak stimulus elicits one antidrome blaze; to stronger stimulus the response may be triphasic; antidrome, homodrome, antidrome. The first and antidrome response is a large effect and soon over, the galvanometer spot flies off and quickly returns to zero and beyond, indicating the second and homodrome effect, which is a prolonged change lasting about two minutes and slowly subsiding, the second effect is often larger than the first.

The blaze is a local effect, as shown in experiment on March 22, where it is abolished by strong tetanus at one spot, but found to persist in other parts on turning the bladder round.

The blaze is abolished by boiling the gall bladder or by subjecting it to strong chloroform vapour, or by tetanus.

Gall Bladder. Experiment of March 3, 1904.

Excitation by Single Break Induction Shocks from Berne Coil.

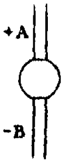
	Strength of excitation.			Response.	
Coil at	1000	−	gave	+0·0012 volt.	Gall bladder had a piece of liver under it
	,,	+	,,	−0·0037	
	,,	+	,,	−0·0080	Gall bladder placed freely between electrodes
	,,	−	,,	+0·0060	
Shunt $\frac{1}{5}$	,,	−	,,	+0·0073	
	,,	+	,,	−0·0080	
	,,	+	,,	−0·0060	
	,,	+	,,	−0·0020	
	,,	−	,,	+0·0012	
	5000	−	,,	+0·0040	
	,,	+	,,	−off	+off
Shunt $\frac{1}{10}$	,,	+	,,	−0·0123	+0·0030
Shunt $\frac{1}{50}$	10000	+	,,	−0·0133	
Shunt $\frac{1}{10}$	,,	−	,,	+0·0033	−0·0025 +
	,,	−	,,	+off	−off
	,,	−	,,	+0·0033	−0·0046
	,,	+	,,	−0·0250	
	1000	+	,,	−0·0003	
	,,	−	,,	Nil	
	5000	−	,,	+0·0020	
	,,	+	,,	−0·0030	
Shunt $\frac{1}{5}$	,,	+	,,	−0·0025	
	,,	−	,,	+0·0015	
	10000	−	,,	+0·0030	
	,,	+	,,	−0·0025	
	,,	−	,,	+0·0025	
Shunt 1	10000	+	,,	−0·0022	
		−	,,	+0·0015	
		−	,,	+0·0011	

Gall Bladder (March 5, 1904).

Coil at.				Response.	Electrodes.
					N.C. +0·0006.
S.s.	1000	+	=	−0·0008	
		−	=	+ off	10000 − = +0·0002
Shunt $\frac{1}{10}$	,,	−	=	+0·0100	,, + = −0·0001
		−	=	+0·0110	
		+	=	−0·0020	

Coil at.		Response.		Electrodes.
1000 +	=	– 0·0020		
–	=	+ 0·0090		
5000 +	=	– 0·0090	+ 0·0080	
–	=	+ 0·0020	– 0·0300	+ 0·0060
–		+ 0·0060	– 0·0080	+ 0·0020
–		+ 0·0080	– 0·0030	
–		+ 0·0080	– sinking	
+		– 0·0040	+ 0·0080	
10000 –		+ 0·0180	– 0·0060	+ off
+		0·0272		
–		+ 0·0172	– 0·0081	+ 0·0030
–		+ 0·0200	– 0·0054	+ 0·0030
+		– 0·0127	+ 0·0054	– 0·0020
+		– 0·0114		
–		+ 0·0085		
–		+ 0·0071	– 0·0015	
5000 +		– 0·0071		
–		+ 0·0035	– 0·0014	
+		– 0·0064		
–		+ 0·0050	– 0·0014	
1000 –		+ 0.0007		
+		– 0·0009		
(Boiled)				
1000 +		nil		
–		nil		
5000 –		+ 0·0002		
+		– 0·0001		
10000 +		– 0·0003		
–		+ 0·0004		

Another Gall Bladder (March 5).



1000 +	=	– 0·0005	
–	=	+ 0·0018	
5000 –	=	+ 0·0091	
+	=	– 0·0075	
10000 +	=	– 0·0087	
–	=	+ 0·0081	The responses are not so lasting as they were
5000 –		+ 0·0054	
+		– 0·0040	

Gall bladder put under $CHCl_3$ in a glass chamber of about 1 inch cubic space. $CHCl_3$ on cotton wool attached to top of chamber by modelling wax. After $\frac{1}{4}$ hour strong chloroform vapour—

5000 – = nil
+ = nil

Gall Bladder (March 9).

Coil at.		Response.	
S.s. 1000 +	=	– 0·0005	
„ –	=	+ 0·0019	
5000 +	=	–	
„ –	=	+ 0·0061	
„ +	=	– 0·0063	
10000 +	=	– 0·0076	+ 0·0005
„ –	=	+ 0·0076	– 0·0005
5000 –		+ 0·0005	– 0·0002
„ +		– 0·0009	
10000 +		– 0·0015	
„ –		+ 0·0012	

Gall Bladder (March 9).

Coil at.			
S.s. 1000 +	– 0·0012		
„ –	+ 0·0020		
5000 –	+ 0·0060		
„ +	– 0·0023		
1000 –	+ 0·0076		
„ +	– 0·0069		
5000 +	– 0·1110	+ after effect then	– 0·0020
„ –	+ 0·0110	– 0·0040	
10000 –	+ 0·0080	Interval then	– 0·0020
„ +	– 0·0060	+ 0·0003	

After chloroform—

5000 +	nil
10000 +	– 0·0001
„ –	nil.

Envelope examined gave no effects and looked dried up; no sign of blood-vessel usually seen.

A. *Gall Bladder* (March 10, 1904).

Coil at.		Response.		
S.s. 1000 +	=	−0·0040		
−		+0·0100		
5000 −		+0·0140	−0·0100	
+		−0·0200	+0·0020	
10000 +		−0·0280	+0·0010	−0·0040
−		+0·0260	−0·0060	

Gall Bladder (March 22).

		Response.		Electrodes.
N.C. (accidental or normal current) = +0·0004 volt				10000 + = −0·00004
S.s. 1000 +	=	nil		= +0·00004
,, −	=	+0·0002		
5000 +	=	−0·0020	+0·0002	
,, −	=	+0·0016	−0·0015	Returning slowly
10000 −	=	+0·0050	Returning slowly, then −0·0009	
,, +	=	−0·0040	+0·0002	
,, +	=	−0·0040		
½ min. tet.				
Coil at 10000 +	=	+0·0015		

After strong tetanus.

S.s. 5000 −	=	+0·0000
10000 −	=	+0·0003
,, +	=	−0·0001
5000 +	=	nil
Tet. ,, +	=	+0·0003
S.s. 10000 −	=	+0·0001

The bladder was turned round in order to expose two fresh surfaces to the electrodes.

N.C. +0·0015, decreasing to 0.

Coil at.				
S.s. 5000 −	=	+0·0007	−0·0002	
10000 −	=	+0·0010	−0·0001	
+	=	−0·0008		−
5000 +	=	−0·0004		

1 minute tetanus

Tetanus at 10000 +

S.s. 10000 +	=	−0·0001
,, −	=	+0·0000

Turned round again to spots previously tetanised.

Coil at.	
S.s. 10000 +	nil
„ −	nil

Gall Bladder (March 24).

	Coil at.		Response.		
	S.s. 1000 +	=	−0·0022		
	−	=	+0·0020	−0·0007	+0·0014 Very slowly subsiding
Shunt $\frac{1}{5}$	−		+0·0013	−0·0003	+0·0011
	+		−0·0038		
	5000 +		−0·0077	+0·0011	Remaining, then falling to −0·0011
Comp. +0·0006	−		+0·0061	−0·0022	+0·0011
Comp. +0·0008	10000 −		+0·0072	−0·0022	
„ +0·0015	+		−0·0088	+0·0005	Back to zero, and falling −0·0005

After 1 hour interval.

10000 +	−0·0069
−	+0·0033

Large Gall Bladder (August 3).

Coil at.		Response.		
S.s. 1000 +	=	−0·0024	+0·0019	Remaining and falling to −0·0010
„ −	=	+0·0012	−0·0027	Returning rapidly to +0·0005 subsiding slowly
„ −	=	+0·0010	−0·0031	+0·0002 subsiding slowly
„ +	=	−off. Remaining and subsiding in 2 minutes		
„ −	=	+0·0027	−0·0006	+0·0019

Gall Bladder (August 11).

S.s. 1000 +	=	−0·0009	+0·0016	Remaining for about 2 minutes −0·0005
−	=	+0·0083		
+	=	−0·0033	+0·0050	−0·0017
5000 +	=	−0·0150	+0·0033	−0·0017
−	=	+0·0133	−0·0006	
10000 −	=	+0·0070	−0·0033	Remaining
+	=	−0·0083	+0·0033	„

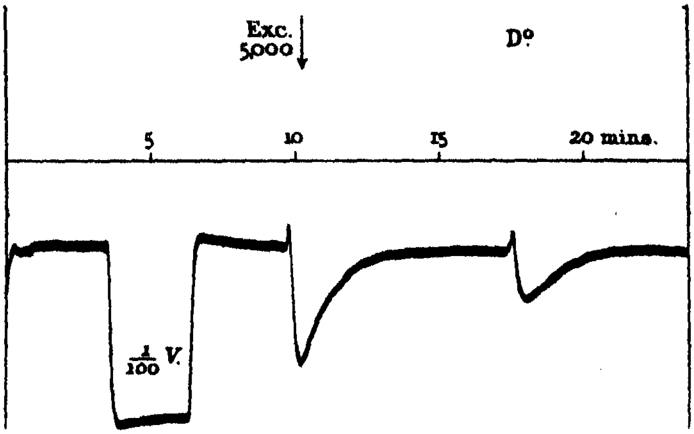
Gall Bladder.

1000 + = −0·0010
− nil
+ = −0·0016
− = nil
5000 − = + off scale, then − off remaining and returning in 2 minutes
− = + 0·0108 − 0·0022
+ = − 0·0108 Slowly returning
− = + 0·0100

September 29.

1000 − = + 0·0011 − 0·0003
+ = − 0·0021
5000 + = − 0·0117 + 0·0017
− = + 0·0112 − 0·0008 + 0·0003

Fig. 1.



Photograph of Galvanometer Record of the Blaze-currents of Gall Bladder. Deviation of $\frac{1}{100}$ volt.

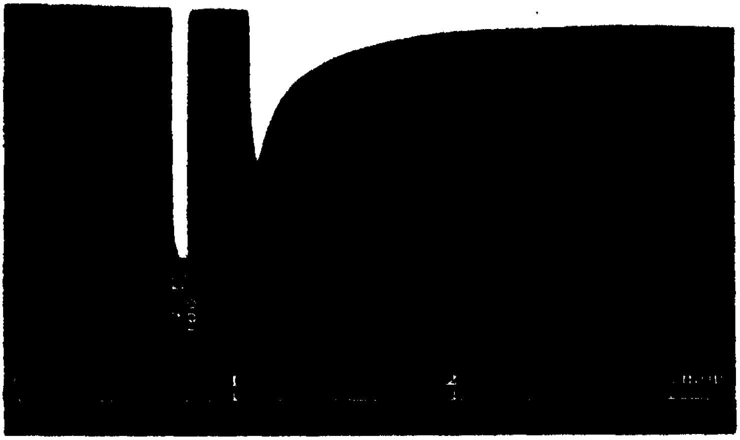
Coil at 5000 + = −0·0010 + 0·0064 volt
" + −0·0010 + 0·0028

In this case the blaze is diphasic, the second phase being larger and more lasting than the first, which is very characteristic.

At Dr. Alcock's suggestion I syringed out the gall bladder and filled it with NaCl solution, 0·6 per cent., and then tested it; the effects still occurred in the some order and almost same magnitude, showing that they were due to action in the enveloping gall bladder itself and not to the bile contents. (See experiments of May 7.)

I am indebted to Dr. Alcock for sections of the gall bladder of the frog and cat which he kindly prepared for me, and to Mr. Gordon Webb for enlarged micro-photographs of the same. The gall bladder of the frog consists of a single layer of columnar nucleated cells, and layers of smooth muscle fibres with connective tissue. The bladder of the frog is quite round and the layer of columnar cells lies flat, whereas in the cat the bladder is a long-shaped body with the layer of columnar cells thrown into folds, and outside the smooth muscle

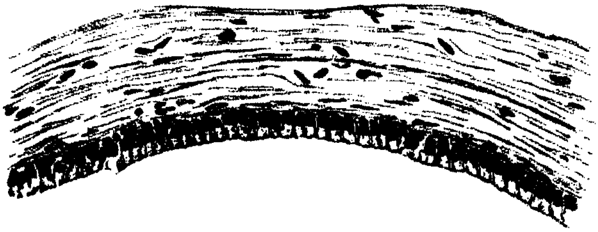
FIG. 2.



Photograph of Electrometer Record of the Blaze Currents of Gall Bladder. Deviation of $\frac{1}{100}$ volt.

Coil at 5000 + = −0·0060 volt.

FIG. 3.



Section of Frog's Gall Bladder, showing Inner Mucous Layer of Columnar Epithelium, and Outer Layers of Smooth Muscle Fibres. (Enlarged 2500 diameters and Photographed by Mr. H. Gordon Webb, Assistant Demonstrator of Anatomy in St. George's Hospital Medical School.)

fibres is a layer of connective tissue. The simplicity of structure in the frog may perhaps account for the large electrical changes observed; in the cat's gall bladder there is little or no response to stimulus.

Gall Bladder Washed out with Salt Solution and then Tested (May 7).

			Response in voltage.	
Coil at S.s.	5000 −	=	+0·0020	−0·0010
	+	=	−0·0003	
	10000 +	=	−0·0010	
	−	=	+0·0030	−0·0005
	−	=	+0·0005	−0·0001

The Gall Bladder syringed out and filled with Salt Solution.

Coil at	10000 +	=	− off	
Shunt $\frac{1}{8}$	+	=	−0·0060	
		=	+0·0050	
	5000	=	+0·0020	−0·0005
	+	=	−0·0022	+0·0001

The bladder is now cut open and spread on electrode with mucous inner surface to A, the upper electrode.

Coil at	10000 +	=	−
		=	+
		=	+
	+	=	

Tested by Waller's ABC method,* the response at both poles is found to be antidrome. In some cases the response is diphasic at the anode, and diphasic at the kathode, see Experiment of May 7th.

By this method the local reactions at anode or kathode can be examined; C is an indifferent point at which an electrode is placed which has not been excited. By means of a switch key the excitation is made through electrodes at points A and B. Any initial current through AC is compensated if it is wished to examine A, and any initial current through BC is compensated if it is wished to examine B. It sometimes happens that AC and BC require compensation in the same direction and of the same magnitude, and then it is permissible to switch the key on to either one or the other, and examine the direction of the current; in the following experiments dotted lines signify that this has been done.

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* On "Skin Currents," 'Roy. Soc. Proc.,' vol. 69, p. 181.

Gall Bladder tested by Dr Waller's ABC Method.

Excitation through BA and lead-off through BC or AC.

B C A

S.s. 1000 ←——————

——→ +0·0142

Remaining and gradually diminishing.

——————→

←—— −0·0019

1000 ——————→

←—— −0·0062

———————

——→ +0·0028

Compensation current.

5000 ←——————

BC = −0·0007 ——→ +0·0075

CA = −0·0008 ·········→ +0·0091

·········→ +0·0094

On changing key to CA the deflection of galv. is further +0·0016 returning to BC sends it further +.

——————→

←—— −off, and back to +0·0010

———————

←—— −0·0075

5000 − ←——————

——→ +0·0150

5000 + ——————→

←—— −0·0075

·········→ +0·0020

←········· −0·0006

Changing to CA sends it +2°, and BC is found to be −6° without shunt.

5000 − ←——————

——→ +0·0150

·········→ +0·0110

Changing to BC lessens the + effect by 4° (shunt $\frac{1}{8}$) = 0·0040

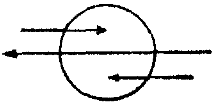
5000 + ——————→

←—— −0·0045 Followed by +0·0025

BC = − 0·0010 5000 ————→
CA = − 0·0010 ←—— − 0·0043 Changing to
: ⋯⋯→ + 0·0033 CA = + 3°

BC = − 0·0014 10000 + ————→
CA = − 0·0011 ←—— − 0·0032
⋯⋯→ + 0·0003
⋯⋯→ + 0·0003

After the effect − 3° (0·0032) has passed off, I unshunt and find that with no shunt BC = + 3° CA = the same 3° +



10000 ←————
——→ + 0·0028
←⋯⋯ − 0·0090
⋯⋯⋯⋯

Changing to CA suddenly, the same deflection persists, but soon falls to − 8°. Changing to BC brings the spot to 0

10000 ←————
CA = + 0·0020 ——→ + 0·0015

BC = − 0·0005 10000 ————→
CA = + 0·0020 ←—— − 0·0015
←⋯⋯

On taking off the compensation, + 0·0020, and changing to BC, spot returns to 0 and goes − 4°

10000 ————→
CA = + 0·0018 ←—— 0·0015

Another Gall Bladder.

	5000 −	+ off	− off
Shunt $\frac{1}{5}$	„ −	+ 0·0078	− 0·0005
	„ +	− 0·0042	+ 0·0052
	10000 +	− 0·0063	+ 0·0050

(First effect quickly over, second effect slowly subsiding.)

− + 0·0078 − 0·0011

	B C A	Response.	
Coil at 5000	←————		
	——→	+ 0·0050	− 0·0011
	←——	− 0·0011	
	←————		
	————→	+ off	− 0·0017

	B	C	A	Response.	
Coil at 5000	←—	——	—		
	—	→		+ off	– 0·0009
	←—	——	—		
		—	→	+ 0·0017	No after effect
	—	——	→		
		←	—	0·0020	Slowly subsiding

1½ hour later—

	B	C	A	Response.
5000	+ =	– off		+ off
Shunt ⅕	+	– 0·0016		+ 0·0042
	–	+ 0·0068		
5000	←—	——	—	
		—	→	+ 0·0002 – 0·0004
– 0·0008	←	—		
	—	——	→	
After 0 changed to BC		←	—	– 0·0015 and return to 0
terminals – 0·0009	←	—		

BC effect – 0·0009 remains and subsides slowly; the CA effect – 0·0015 disappeared quickly, for the spot returned quickly to 0

	B	C	A	Response.
	—	——	→	
– off, slowly subsiding	←	—		
to + 4		—	→	+ 0·0004

Slight + effect on changing to CA, but – effect on changing back to BC; the – effect at BC has now subsided and is going +

	B	C	A	Response.	
	←—	——	—		
	—	→		+ off	– 0·0010
		←	—	– 0·0005 after the BC has returned to 0	
	←—	——	—		
	—	→		+ 0·0036	– 0·0011
		—	—	0	
10000	—	——	→		
		←	—	– 0·0031	
	—	→		+ 0·0005	
		←	—	– 0·0005	
	—	——	→		
	←	—		– 0·0002	
		—	—	0	

Gall Bladder (May 7).

		5000 +	−0·0030	
		−	+0·0030	
		Kathode	Anode	
(1)		←		
		→	+0·0030	
(2)		←		
		→	+0·0023	
		Anode	Kathode	
(3)		→		
		←	−0·0012	
(4)		→		
		←	−0·0008	
(5)		→		
		←	−0·0008	
		Kathode		
(6)		←		
		←	−0·0006	
		Kathode		
(7)		←		
		←	−0·0004	
(8)		←		
		→	+0·0013	
(9)		←		
		→	+0·0007	−0·0002
	+0·0025	→		
(10)		←		
	−0·0001	←		
		←	−0·0030	
(11)		←		
		→	+0·0006	−0·0001
		→	+0·0030	
		Kathode		
(12)		←		
	−0·0001	←		
		←	−0·0040	

In experiment, May 7, some of the responses from the kathode are homodrome, *e.g.*, excitations (6), (7) and (12); in the last there is found to be a homodrome response from the anode which also appears slightly in (11) after the usual antidrome.

Gall Bladder Attached to Liver.

Compensation.	Coil at 5000			
	−	+0·0094	−0·0011	+0·0033
+0·0006	+	−0·0100	+0·0011	
	+	−0·0036		
	−	+0·0054	−0·0038	

Compensation.				
+0·0005	10000	−	+0·0100	−0·0038
,,		+	−0·0161	
+0·0003		+	−0·0130	
−0·0002		−	+0·0061	−0·0034

Excitation through BA, lead off from A or B, and an indifferent point, C.

		B C A		
Coil at	1000	←————		
		——→	+0·0001	
		Anode		
,,	5000	←————		
		←——	−0·0015	
	,,	————→		
		←——	−0·0037	
		Anode		
	,,	←————		
		←——	−0·0012	
	,,	————→		
		←——	−0·0037	
	10000	←————		
		——→	+0·0065	−0·0022
	5000	←————		
		——→	+0·0015	−0·0007
	,,	←————		
		——→	+0·0035	
		Anode		
	,,	—— ——→		
		——→	+0·0020	
		Anode		
	10000	————→		
		——→	+0·0032	
	,,	←————		
		——→	+0·0030	

Excitation through BA, and lead off through BA.

5000	←————	
	————→	+0·0070
,,	————→	
	————→	+0·0030

Excitation through BC, and lead off through BC, ditto CA.

5000	——→		
	←——		−0·0070
,,		←——	
		——→	+0·0050

In this experiment some of the responses from the anode are homodrome. A single shock with coil at 5000 − gives −0·0015 from the anode. The stronger excitation with coil at 10000 calls out the antidrome response +0·0065 and then the homodrome response from the anode −0·0022, and then the weaker excitation at 5000 gives the same responses in a lesser degree +0·0015 −0·0007.

Same Gall Bladder separated from Liver.

	B C A	Response.	
Coil at 5000	B ————→ A		
	B ←———— A	−0·0050	+0·0040
	B - - - - → A		
	B ← - - - - A	−0·0020	+0·0025
	C ——→ A		
	C ←—— A	−0·0007	+0·0015

Envelope

5000 + = −0·0004 +0·0003
− = +0·0006
10000 − = +0·0008
+ = −0·0006

Liver (April 30).

5000 − = +0·0010
+ −0·0020
10000 + = −0·0036
− = +0·0026

Gall Bladder alone.

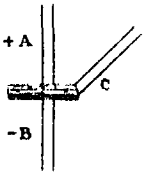
5000 −	+0·0250	Then sinks to −0·0080	
+	−0·0100	+0·0050	Sinking back to −0·0040
−	+0·0250	−0·0100	
+	−0·0050	+0·0060	

Slice of envelope gave no response.
Contents of gall bladder gave no response.

It is a very easy matter to demonstrate the blaze-currents on the frog's gall-bladder, because the organ can be separated and placed between electrodes without injury; but it is a difficult matter to cut out a piece of the round bladder and place it on electrodes without injuring the delicate tissue. It is necessary, however, to do this in order to study separately the mucous and serous surfaces. I found the most convenient procedure was to cut the bladder across with scissors, the bladder collapses, but the piece cut off rests on the blade of the scissor and can be gently drawn by a brush on to the soft china clay electrode, so that the inner epithelial surface, which laid on the scissor blade, now rests on the electrode; the other electrode can be now applied to the outer smooth muscle fibre surface. If the piece of bladder is sufficiently large a third electrode can be applied to its edge and the effect of stimulation at both surfaces studied by Waller's ABC method.

In the experiments of March 10 the blaze was directed from the mucous to the serous surface and was of considerable magnitude, but the sixth excitation elicited a response in the antidrome direction before giving one from mucous to serous. In experiment of July 21 there is also blaze from mucous to serous.

The following figure gives a plan of the position of the electrodes and tissue in the ABC experiments. Unless otherwise stated in the following tables the + sign signifies from mucous to serous and – signifies from serous to mucous.



A. *Envelope of Bladder* (March 10).

5000 –	– 0·0008	
+	– off	
+	– 0·0125	
10000 +	– 0·0160	
–	– 0·0020	
–	+ 0·0020	– 0·0100
+	– 0·0060	

– Means from mucous to serous.

Gall Bladder.

5000 –	+ 0·0066
„ +	– 0·0058
10000 +	– 0·0083
„ –	+ 0·0100

Envelope (March 24).

5000 –	+ 0·0004
„ +	– 0·0009
10000 –	+ 0·0010
„ +	– 0·0025
„ +	– 0·0025

The layers were not properly separated.

B. *Envelope of Gall Bladder.*

5000 + = - 0·0045
10000 + - 0·0047 First trial of envelope
- + 0·0018 is doubtful as to
single layer.

Envelope of Gall Bladder (May 7).

5000 + - 0·0008
- + 0·0001

June 7.

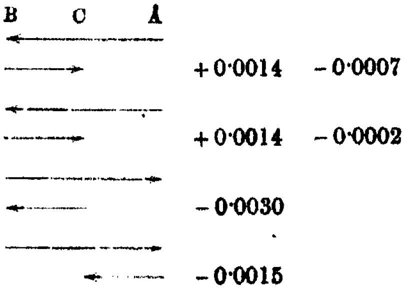
Volt.
Electrodes A and B. N.C. = 0. 1/1000 = 9
S.s. 10000 + = 0
" " - = 0
Electrodes B and C. N.C. = + 0·0004
S.s. 10000 + = 0
" " - = 0

Gall Bladder.

N.C. + 0·0027. B to A.

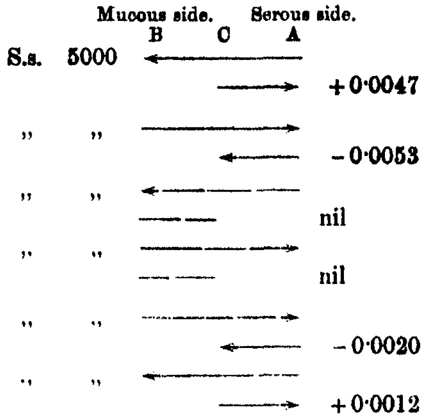
Shunt $\frac{1}{5}$. S.s. 5000 + = - off 1/100 volt = 14
Shunt $\frac{1}{10}$. " " + = - 0·0160 " = 5
" - = + 0·0260
" 1000 - = + 0·0050
" + = - 0·0043
Shunt $\frac{1}{5}$. 5000 + = - 0·0036 " = 14
Shunt $\frac{1}{10}$. 10000 + = - 0·0071
" - = + 0·0030

S.s. 5000



Envelope of Gall Bladder.

S.s. 5000 + = −0·0020
− = +0·0030



Gall Bladder—entire (June 10).

S.s.	5000 − =	+0·0075	−0·0087	
	„ +	−0·0150	+0·0125	
	1000 +	−0·0020		
	„ −	+0·0013		
	5000 −	+0·0125	−0·0110	+0·0010
	+	−0·0100	+0·0100	

Portion of envelope only, with electrodes placed one on mucous, the other on serous side.

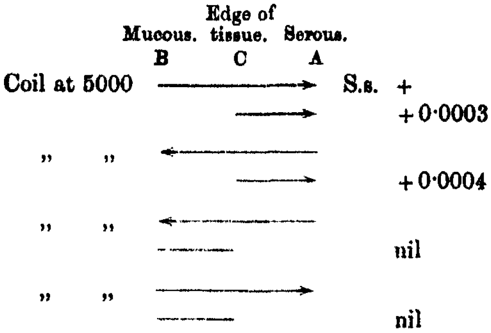
S.s.	5000 −	+0·0007	
	„ +	−0·0031	
	−	+0·0012	
	+	−0·0010	+0·0003
	−	+0·0015	
	−	+0·0015	
	+	−0·0014	

Slice of Gall Bladder Envelope (July 12).

S.s. coil at 5000 + = −0·0030
= +0·0030

Slice of Gall Bladder Envelope (July 14).

S.s. 5000 – = + off scale.
+ = + 0·0008
10000 + = – 0·0009 + 0·0008
„ – = + 0·0045
+ = – 0·0011 + 0·0003

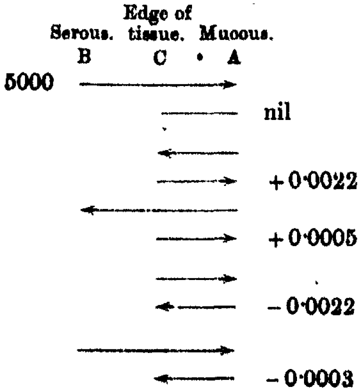


Envelope of Gall Bladder.

5000 – = + 0·0003 – 0·0007
+ = – 0·0001
10000 + = – 0·0003 + 0·0003
– = + 0·0010

Envelope (August 3).

5000 – = + 0·0022
+ = – 0·0010



Serous. B	Edge of tissue. C	Mucous. A	
——	——	—→	
←—	——		– 0·0007
←—	——	——	
——	—→		+ 0·0008
←—	——		
- - -	- -→		+ 0·0020
——	—→		
←—	——		– 0·0015

Envelope (August 11).

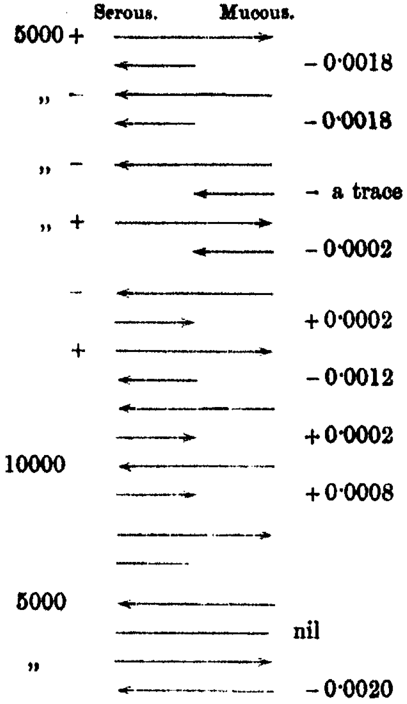
S.s. 5000 – = + 0·0005 Sinking to – 0·0010 and very slowly returning after remaining 2 minutes at – 0·0005
,, + = – 0·0003
10000 + = – 0·0005
,, – = + 0·0008

Envelope of Gall Bladder.

	B Mucous.	C	A Serous.	
Coil at 5000	——	——	—→	
		←—	——	– 0·0004
	←—	——	——	
		——	——	nil
	←—	——	——	
	——	——		nil
	——	——	—→	
	——	——		nil
		- - -	- - -	
		——	—→	+ 0·0002
	——	——	—→	
		←—	——	– 0·0006
10000	——	——	—→	
	←—	——	——	– off scale lasting 2 minutes and returning to zero
	←—	——	——	
	——	——	—→	+ 0·0003
	——	——	—→	
	←—	——	——	0·0011 lasting 2 minutes

Envelope of Gall Bladder (July 21).

5000 – = – 0·0010 (from mucous to serous)
+ = – 0·0020



Slice of Gall Bladder (July 14).

Coil at 5000 – = + off scale
" + = + 0·0008
10000 + = – 0·0009 + 0·0008
– = + 0·0045
+ = – 0·0011 + 0·0003

In this experiment the envelope was placed so that the + or positive deflection signified a blaze from mucous to serous surfaces. In the five cases given the first is a large effect in the usual antidrome direction, being an addition of the mucous to serous blaze to the negative polarisation characteristic of this tissue, the second is the mucous to serous effect without negative polarisation, the third stimulation being stronger brings out a negative polarisation effect (presumably from the smooth muscle fibres), and then the positive effect from mucous to serous. The last strong stimulation brings out a negative plus the positive effect as in the first case.

The experiment of July 14 agrees with the experiment of July 21 in that the direction of blaze was from mucous to serous.

The envelope of the gall-bladder behaves like all the mucous membranes in that there is a tendency for the blaze current to pass from mucous to serous tissues, but this effect is constantly masked by the negative or antidrome blaze peculiar to this organ. The ABC method shows that the serous surface displays the antidrome blaze more readily than the mucous surface.

Envelope of Gall Bladder.

Coil at 5000 − = +0·0003 −0·0007
+ = −0·0001
10000 + = −0·0003 +0·0003
− = +0·0010

August 3.

5000	→		→	
	—	nil	←	−0·0003
	←		→	
	—	nil	←	−0·0008
	←		←	
	→	+0·0022	→	+0·0009
	←		←	
	→	+0·0005	→	+0·0019
	→		→	
	←	−0·0022	←	−0·0017

August 11.

Envelope.			*Envelope.*			
5000 +	=	−0·0008	5000 −	=	+0·0005	−0·0009
−	=	+0·0002	+	=	−0·0002	
10000 −	=	+0·0005	10000 +	=	−0·0006	
+	=	−0·0007	−	=	+0·0008	

These experiments show the gall bladder to be an organ whose tissues possess great "chemical lability," the kathode of the single induction shock is more effective than the anode whether the stimulus occurs in the smooth muscle fibres or in the columnar mucous epithelium, so that the blaze is first post kathodic, then post anodic. Occasionally the usual mucous to serous blaze occurs, but of the two components of the structure, the smooth muscle fibres appear to give the blaze current more readily than the columnar epithelium.

The gall bladder presents a very striking instance of the equivocal or antidrome blaze current.

In conclusion I should like to be allowed the pleasure of thanking my husband for continual help and sympathy in my work, and to record my appreciation of and gratitude for the method of investigation, and simplified arrangement of electrical apparatus which renders it easy to study the many fascinating problems of animal and vegetable electricity.

"On the Compressibility of Gases between One Atmosphere and Half an Atmosphere of Pressure." By LORD RAYLEIGH, O.M., F.R.S. Received January 17,—Read February 2, 1905.

(Abstract.)

The present memoir contains a detailed account of the observations referred to in the Preliminary Notice of February, 1904. In addition, results are now given for air, carbonic anhydride, and nitrous oxide. In the following table are recorded the values of B for the various gases at specified temperatures, B denoting the quotient of the value of *pv* at half an atmosphere by the value at the whole atmosphere :—

Gas.	B.	Temperature.
Oxygen	1·00038	11·2
Hydrogen	0·99974	10·7
Nitrogen	1·00015	14·9
Carbonic oxide	1·00026	13·8
Air	1·00023	11·4
Carbon dioxide	1·00279	15·0
Nitrous oxide	1·00327	11·0

By means of a formula given by D. Berthelot the compressibilities at 0° C. are inferred, and applied to deduce the ratio of densities as they would be observed at 0° C. under very low pressures. According to Avogadro's law these are the relative molecular weights. From the densities of nitrogen and oxygen we get $N = 14·008$, if $O = 16$. Again, from the densities of oxygen and nitrous oxide we find $N = 13·998$. The former is probably the more trustworthy.

"The Theory of Photographic Processes: On the Chemical Dynamics of Development." By S. E. SHEPPARD, B.Sc., and C. E. K. MEES, B.Sc. Communicated by SIR WILLIAM RAMSAY, K.C.B., F.R.S. Received December 20, 1904,—Read February 2, 1905.

(Presented in Theses for the Degree of B.Sc. by Research in the University of London.)

Historical and Introductory.—The following work was undertaken with the view of applying physico-chemical methods to the study of photographic development. Although, as has been pointed out by Ostwald, the problem falls in the province of chemical dynamics, but little systematic work has been done from this point of view. The increasing use of gelatino-bromide films in connection with radiation phenomena make a greater knowledge of the laws describing development and exposure very desirable, while the importançe of the photographic industry needs no comment. The following brief historical introduction is necessary in order to sum up the progress made and the terminology in use:—

In 1878, Sir W. Abney* showed that the black reduction product in development was metallic silver. He introduced the measurement of the transparency of the deposits by means of a photometer, and proposed as the relation between the mass of silver reduced and the transparency a form of the law of error. In 1890, Messrs. F. Hurter and V. C. Driffield† made a systematic survey of exposure and development in which a new terminology was introduced and several very important conceptions and results. These were extended in 1898 in a second paper dealing largely with development.‡ They considered that the ordinary exponential law§ for the absorption of light in homogeneous media held for the photographic image and confirmed this view experimentally. They gave the following terminology, which has been generally accepted:—

Transparency ... $T = \frac{I}{I_0} = \frac{\text{Intensity transmitted}}{\text{Intensity incident}}$,

Opacity .... $O = \frac{I_0}{I} = \frac{1}{T}$,

Density .... $D = -\log_e T = \log_e O$.

D, the density, is for convenience usually taken as $-\log_{10} T$, and according to Hurter and Driffield is directly proportional to the mass of silver per unit area.[*]

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* 'Phil. Mag.,' 1878; also 'E. B.,' 10th edit., art. "Photography."

† 'Journ. of Soc. of Chem. Industry,' May, 1890.

‡ 'Photographic Journal,' 1898; Eder's 'Jahrbuch f. Phot.,' 1899.

§ Bunsen and Roscoe 'Pogg. Ann.,' vols. 95 to 100.

References to the work on exposure and development will be made in the course of the present work. Many of their conclusions have been controverted[†] chiefly from isolated experiments. Nevertheless, their method of sensitometry has been nominally adopted for commercial purposes in England. It has, however, been attacked by Dr. Eder[‡] in the course of his important researches on sensitometry.

The authors have dealt elsewhere with the question of sensitometry, with the result of confirming in general the results of Hurter and Driffield.

Applications of physico-chemical doctrine to photographic phenomena may be found in the short-lived 'Archiv f. wiss. Phot.'[§] and, in especial, Abegg's "silver-germ" theory of exposure and development. This is dealt with later.

All developers are, chemically speaking, reducing agents, but the converse does not hold. In connection with this, Bredig[‖] has pointed out the importance of the "reduction potential"[¶] as a function of the developer. However, as there is no strict proportionality between "potential" and reaction velocity,[**] other conceptions are necessary, if the "efficiency" of developers is to be measured. The relation, as has been pointed out, may be conceived as analogous to Ohm's law, velocity $= \frac{\text{potential}}{\text{resistance}}$,[††] and this "resistance" in chemical reactions is a term difficult to define or measure.

The chemistry of organic developing agents has been extensively investigated by Messrs. Lumière and Dr. Andresen,[‡‡] to whom we owe the following rule:—All organic developers are substituted aromatic derivatives, containing two of the groups OH and NH_2, joined by an ortho- or para- linking, the meta- bodies not acting as developers. Andresen[§§] has pointed out the analogy between these bodies and the simple inorganic types, O_2H_2, hydrogen peroxide, N_2H_4, hydrazine, and $NH_2 \cdot OH$, hydroxylamine, all of which function as developers.[*] It seems possible that the quantitative investigation of development might throw light on the affinities of a large group of organic bodies.

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[*] *Cf.* Eder: 'Beiträge zür Photochemie u. Spectral-analyse,' 1904; Luther, 'Zeit. f. Phys. Chem.,' 1900 (*Ref.*) recommends the term "Extinction," instead of the anomalous "density," as this quantity is the same as the "Extinction coefficient" introduced by Vierordt in absorption-photometry.

[†] For a bibliography of this controversy, see C. E. K. Mees and S. E. Sheppard, "Instruments for Sensitometry," 'Phot. Journ.,' vol. 44, No. 7, p. 222; and "On Sensitometry," *ibid.*, No. 9.

[‡] *Loc. cit. supra*, or 'Sitzber. d. Wien. Akad.,' vol. 113, 1899, sect. A.

[§] 'Archiv f. Wiss. Phot.,' 1899 to 1900.

[‖] Eder's Jahrbuch, 1895.

[¶] Bancroft and Neumann, 'Zeit. f. Physik. Chem.,' 10, 857. Nernst, 'Theoret. Chem.,' 4te Auflage, p. 710.

[**] Ostwald, 'Lehrbuch,' 2te Bd., 2te Tl. (2te Auflage).

[††] Nernst, 'Theoret. Chemie.,' 4te Auflage, p. 656.

[‡‡] 'Photo. Bulletin,' 1895, *et seq.* Eder's Jahrbuch, 1899 (pp. 140 to 147).

[§§] 'Phot. Corr.,' 1899, p. 212. Eder's Jahrbuch, 1899 (pp. 140 to 147).

Owing to the complications present in organic developing solutions,[†] the reaction was first studied with ferrous salts, those employed being ferrous oxalate, citrate, and fluoride. These can be easily estimated analytically, and disturbing side reactions do not occur to any extent. The methods and conclusions arrived at can then be applied to the study of other developing agents.

Apparatus and Method of Enquiry.—The apparatus used by the authors and other investigators for the investigation of sensitometry and development have been very fully described elsewhere,[‡] so that only a brief description with an account of the errors in working is here necessary.

The progress of the reaction was studied by measuring the density, varying amounts of light action being obtained by means of a special sensitometer.

(*a*) The sensitometer impressed a known gradation of exposure on the plate by means of an accurately calibrated sector-wheel, exposed to a constant pressure acetylene burner.[§]

(*b*) A special thermostat was employed, so that all the chemical reactions involved took place under constant conditions, temperature to 0·1° C.

(*c*) The absorption photometer used was a Hüfner spectrophotometer.[||] The silver deposit had no spectral absorption, but measurements were made in the bright green, the region of maximum luminosity in the visual curve.[¶] The instrument uses two Nicol prisms for polarising the light, and so darkening the comparison field. If θ be the angle of rotation of the analyser, T, the transparency $= I/I_0$ is equal to $\cos^2\theta$, and D, the density (after Hurter and Driffield) is equal to $-\log_{10}\cos^2\theta$. The estimation of the probable error for a single density—the scatter—gave the following result:—The mean probable error from 3·0 to 0·100 was approximately constant at 0·007.[**] As six readings were taken, from 3·000 to 0·100, the figures are trustworthy to three units on the third decimal place.

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[*] Le Roy., 'Bull. Soc. Franç. Phot.,' 1894, vol. 23. Andresen, 'Phot. Corr.,' vol. 36, p. 260.

[†] Mees and Sheppard, 'Zeit. f. Wiss. Phot.,' Bd. II, H. 1, 1904.

[‡] 'Phot. Journ.,' "Instruments for Sensitometric Investigation," vol. 44, 1904, No. 7.

[§] *Loc. cit.*

[||] *Loc. cit.* and 'Zeit. f. Physik. Chem.,' 3.

[¶] Further, the region for maximum sensitiveness for small differences in intensity, Unterschieds-empfindlichkeit, lies, according to Pflüger, between λ 495 and λ 525. 'Ann. d. Phys.,' 4te Flge., Bd. 9, p. 207.

[**] *Cf.* Martens: "Modified König. Spectrophotometer," 'Ann. d. Phys.,' 4te Flge., Bd. 12, 1903. "As long as a_0 does not lie near 0° or 90°, p, the just perceptible difference of brightness of the comparison fields, is constant."

The next consideration is as to how far D represents the mass of silver per unit area. In treating the image as obeying the absorption law, no account is taken of the light diffusely scattered.[*] It is true that so long as all densities are measured at the same distance, the scattered light lost is probably proportional to the scattering surface, *i.e.*, to the density. In this case the result does not affect the form of the curve, for $D = \phi(T) = \phi'$ (mass of silver), but only the slope, *i.e.*, the photometer-constant. But the error due to this cause with the Hüfner instrument is, for negatives, inappreciable. If proper precautions with regard to obstruction of light by the absorption stand are taken, and adjustment made so that the zero does not alter, it is found that the measured density does not alter on changing the distance of the light source. Further, if a diffusing medium, such as milk-glass, be interposed, the density readings are not altered beyond the probable error. On the other hand, if this be done with an undeveloped plate, quite different readings are obtained. When measuring highly diffusing media, such as haloid of silver emulsions, *it is necessary to use a highly diffusing light source, and also to utilise only a narrow strip of the transmitted bundle of rays.* This may be accomplished by means of the carriers described in our former paper.

The Photometric Constant.—As was stated above, Hurter and Driffield showed that the amount of silver per unit area was directly proportional to the density $D = -\log T$ where T is the photometric transparency. This was found for densities from 0·525 to 2·0, the mean value of P being 0·0121, P is the mass of silver in grammes per 100 cms.^{2}, corresponding to a density of 1·0, and is henceforth referred to as the photometric constant. A redetermination of P in 1898 gave $P = 0·0131$ for ferrous oxalate. The photometric constant varies slightly with the developer, especially if organic stain be deposited. Dr. Eder also confirmed this ratio for densities from 0·5 to 2·0, and obtained the value 0·0103 for P (ferrous oxalate). As this relation is of great importance in the theory of development and sensitometry, we made a redetermination, extending the range of densities to 3·5, as it seemed possible divergencies might occur at higher densities. The photometric constant allows quantities of silver to be estimated much below analytical measurement.

Hurter and Driffield, after the necessary density-measurements, removed the film from the plate and dissolved the silver in nitric acid: it was then precipitated as AgCl, and weighed. Dr. Eder converted the silver directly by means of bichromate and HCl into AgCl.

These gravimetric methods are somewhat disadvantageous in dealing with the small quantities of silver present. If plates of small area are used, the ultimate analytical error for so small a quantity of AgCl may seriously affect the results, while with larger plates the irregularity in the developed density, primarily due to coating, causes errors which are only partially compensated by taking many readings over the plate. It would be preferable, moreover, to precipitate the silver as AgBr, both owing to its slighter solubility and the greater weight of precipitate obtained.

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[*] Abney, 'Phil. Mag.,' 1875. C. Jones, 'Phot. Journal,' 1898 to 1899, p. 99.

A preliminary gravimetric determination was made, in order to check the volumetric method subsequently employed. The densities ranged from 2·4 to 3·25 and the value of P obtained was 0·01035.

The volumetric method adopted was Volhard's,[*] with thiocyanate sometimes controlled by the precipitation with KBr. The standard silver solution was N/100 $AgNO_3$, prepared by dissolving 1·6997 grammes pure $AgNO_3$ in water with excess of HNO_3 and made up to 1000 c.c. at 15° C. This was checked by analysis, and two concordant determinations gave the factor 1·001. The standard KCNS, N/100 had the factor 1·017.

Details of the Estimation on Plates.—Half-plates and whole-plates were exposed at 2 to 3 metres, carefully developed, fixed and washed. Very careful washing was necessary in order to extract all soluble salts. They were dried at the standard temperature. The density was measured in 20 to 30 places,[†] and the area; after this the film was removed by dilute HF and soaked in many changes of distilled water, with frequent pressure between filter paper, to remove all soluble salts which might interfere.[‡] The film was then dissolved in slight excess of pure HNO_3, SG 1·49 and the gelatine completely destroyed by heating, as otherwise it interferes with the subsequent titration by forming a pseudo-solution of the precipitate and retarding its aggregation.[§] The solution was made up to 25 c.c. at 15° C. and titrated with N/100 KCNS, using 2 c.c. of 10-per-cent. ferric-am. sulphate as indicator.

The following series is exemplary. Four series of measurements were made in this way, the density ranging from 0·50 to 3·5, and the curve shows that there is no bias throughout the range.

Series IV.

Plate.	Area.	Density.	Titre.	P.
1......	87·2 cms.^{2}	1·438	11·8 c.c.	0·01033
3......	86·7 ,,	2·392	18·7 ,,	0·01019
4......	87·2 ,,	2·067	16·5 ,,	0·01032
5......	87·2 ,,	1·809	14·95 ,,	0·01040
6......	87·2 ,,	1·618	13·1 ,,	0·01022

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[*] *Cf.* Mohr's 'Titrirmethode.'

[†] This was necessary, as variations in the developed density up to 10 per cent. occurred, chiefly due to coating errors.

[‡] *Cf.* Lumière and Seyewetz "On Retention of Hypo," Ref. in 'P. J.,' 1902.

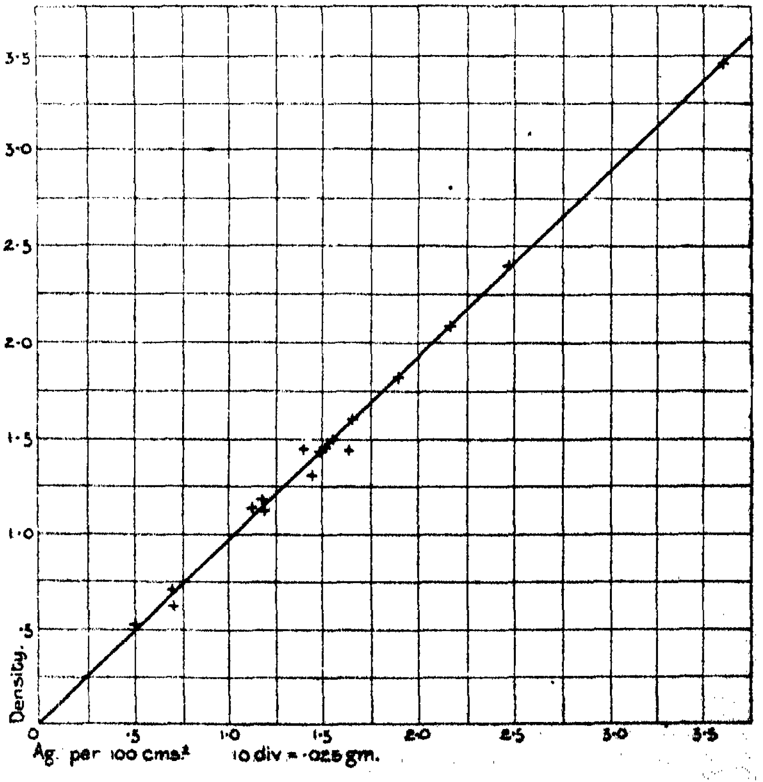
[§] Lobry de Bruyn 'Ber.,' 1902, vol. 35, pp. 3079 to 3082.

The means of all series are as follows :—

I…………	0·01035	Gravimetric.
II…………	0·01012	Volumetric.
III…………	0·01037	„
IV…………	0·01029	„
V…………	0·01040	„

Total mean…… 0·01031 = P for plates employed.

Wratten ordinary emulsion and ferrous oxalate. Curve I shows the directly proportional ratio between the density $D = \log_{10} O$ and the mass of silver per 100 cms.^{2}. The mean value differs materially from that found by Hurter and Driffield, but this may be due (*a*) to a constant error in their photometer; (*b*) to the plates used, as it seems probable that the emulsification of the silver haloid has considerable influence on the "covering power" of the silver subsequently deposited. This "covering power" is, of course, the quantity P or photometric constant.



The extent to which the exponential law holds for gelatine emulsions is of great practical importance, as it provides a rapid and easy method of measuring the amount of substance present. The following experiments indicate that it holds within certain limits.

Table calculated from Hurter and Driffield.

Plate.	AgBr per 100 cms.^{2}	Density.
1.................	0·016 gramme	0·240
2.................	0·031 ,,	0·520
3.................	0·062 ,,	1·000
4.................	0·124 ,,	2·900*

The writers converted silver into AgBr and measured the density in each case. Considering how high the figures are, the results are satisfactory.

Series I.

Density of silver.........	2·023	P, for AgBr = 0·0364.
,, AgBr.........	4·020	

Series II.

Density of silver.........	1·009	P, for AgBr = 0·0393.
,, AgBr.........	2·026	

Comparing these with Hurter and Driffield's numbers, it is obvious that the physical state of the haloid has tremendous influence on the opacity. Considering the importance of this quantity for sensitometry, the constant P seems worthy of investigation in connection with emulsification.

The investigation shows that the density can be accepted as a measure of the mass of silver reduced.

Errors due to Plates.—Unevenness in the coating of the plates introduces a large source of errors. In these researches, Wratten ordinary emulsion specially coated on patent plate glass was used, the edges being rejected. We have to thank Mr. Wratten for the care taken and his readiness in coating experimental plates. Nevertheless, as the following figures show, the error from this source is considerable. Plates similarly exposed and developed, resulted as below :—

	a.	*b.*	*c.*
1	1·364	1·336	1·403
2	1·329	1·342	1·354
3	1·289	1·321	1·247
4	1·287	1·349	1·280
5	1·337	1·375	1·340
Mean	1·3212	1·345	1·325
Greatest dev.	3·2 per cent.	2·2 per cent.	6·0 per cent.

* Probably due to "scatter" error.

From these and other measurements it was calculated that from this cause alone the probable error on a single developed density is 1 per cent.[*] The authors have since constructed an instrument for the more exact coating of plates.

Method of Development and Developer.—The thermostat and plate-holders have already been described. Previous to development, the plates were soaked for 2 to 3 minutes in a tube of distilled water in the thermostat. Development was stopped by plunging the plates in cold water, they were washed, fixed in pure hypo, washed, cleared in dilute HCl, rinsed, wiped with cotton wool, and dried at a uniform temperature.

The developer first used was ferrous oxalate. A physico-chemical investigation had shown that the iron was present as a complex anion[†] $Fe(C_2O_4)_2$, which is stable in the presence of excess of free oxalate ions, according to the equilibrium

$$Fe(\bar{C}_2\bar{O}_4)_2 \rightleftharpoons FeC_2O_4 + \bar{C}_2\bar{O}_4.$$

When the ferrous oxalate is present in solid form, the constant for the above equilibrium is 0·8 at 20° C. The standard solutions employed were

A. $FeSO_4$ …… 278 grammes per litre, molecular,
B. $K_2C_2O_4$ …… 184 " "

checked by titration with standard $KMnO_4$.

The developer was always slightly acidified with pure H_2SO_4.

The Velocity of Development.—This was studied by measuring the growth of the density, *i.e.*, the mass of silver, with the time of reaction, in full analogy with other kinetic investigations. The following facts were experimentally proved :—

(*a*) The silver deposited increases rapidly at first, then more slowly, and finally tends to a limit.

(*b*) This limit depends only on the exposure.[‡]

(*c*) The velocity depends upon the concentration of the reducer.

(*d*) A soluble bromide reduces the velocity, but the "slowing off" with time is not so pronounced.

Temperature was always 20°·0 C., unless otherwise stated.

Table I for *a*, *b*, and *c*.

Developer A……	5 c.c. $FeSO_4$,	M/1.	Exposure 10 CMS.
	45 " $K_2C_2O_4$,	M/1.	
" B……	2 " $FeSO_4$,	M/1.	Exposure 50 CMS.
	48 " $K_2C_2O_4$,	M/1.	

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[*] *Loc. cit.*, "Instruments for Sensitometry," 'P. J.,' 1904, No. 7.

[†] 'Proc. of Chem. Soc.,' vol. 21, No. 288, p. 10.

[‡] Apparent exceptions to this law will be discussed in subsequent work.

Table I.

A. Time.	Density.	B. Time.	Density.
5·0 mins.	1·052	5·0 mins.	0·628
10·0 „	1·230	10·0 „	0·987
20·0 „	1·296	15·0 „	1·323
45·0 „	1·444	20·0 „	1·376
90·0 „	1·591	30·0 „	1·528
120·0 „	1·623	90·0 „	2·429

and confirming *a*, *b*, *d*.

Developer, 4·0 c.c. $FeSO_4$, M/1.
40·0 „ $K_2C_2O_4$, M/1.
1·0 „ KBr, N/10.
to 50·0 „ with H_2O.

Table II.

D_6 = 50 CMS.		D_9 = 10 CMS.	
Time.	Density.	Time.	Density.
5·0 mins.	0·256	10·0 mins.	0·522
11·0 „	0·759	15·0 „	0·741
15·0 „	1·001	20·0 „	0·838
20·5 „	1·375	30·0 „	0·939
25·0 „	1·435	40·0 „	1·050
31·0 „	1·541	50·0 „	1·185
40·0 „	1·847	60·0 „	1·212
50·0 „	2·119	75·0 „	1·360
60·0 „	2·148	90·0 „	1·409
70·0 „	2·333	105·0 „	1·574
90·0 „	2·398	135·0 „	1·641
120·0 „	2·398	12 hours	1·641

These facts are in agreement with Hurter and Driffield's statement that development tends to a limit depending upon the exposure. They considered that their results were represented by the formula $D = D_\infty(1 - a^t)$* where D = density at time t, D_∞ = ultimate density, and a is a constant. They stated that this was arrived at "on the idea that the number of silver bromide particles affected by light is greatest in the front layer of the film and decreases in geometrical progression as each successive layer is reached," and "that the developer reduced the particles as it penetrated the film." Apart from the inherent improbability of this process taking place so regularly, it would, as was pointed out by Luggin,† give results in contradiction to the law of constant-density ratios demonstrated later. A conclusive experimental disproof of the hypothesis is given by the fact that a plate exposed from the glass-side develops normally, although in this case the layer containing fewest reduced particles is reached by the developer first.

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* 'J. Soc. of Chem. Ind.,' May, 1890.

† 'Zeit. f. Phys. Chem.,' 23, p. 622.

Table III.

Time.	Density.	K.
11·0 mins.	0·477	0·0210
15·0 „	0·612	0·0217
20·0 „	0·681	0·0193
33·0 „	0·897	0·0197
75·0 „	1·156	
120·0 „	1·156	

For meaning of K, see later.

The mass-time curve is quite normal.

Another theory of development-velocity was proposed by Dr. Abegg,* based on his "silver-germ" theory of the latent image. According to this, the velocity of development, *i.e.*, the number of silver germs deposited in unit time is proportional to the number present at any time. This may be expressed by $v = \frac{dx}{dt} = k(a+b+x)$, where a and b are constant numbers of germs due to exposure and ripening respectively, and x is the number due to development. It is evident that as x increases the velocity should increase, and a steady acceleration should be noticed till the whole film was developed through; in this unmodified form the expression is in obvious disagreement with the facts of development.

Theory of Development.—The investigations of Boguski,† Noyes and Whitney,‡ and especially of M. Wilderman,§ E. Bruner, and Nernst,|| have led to a better understanding of the reaction-velocity in heterogeneous systems, among which the development of silver-bromide naturally stands. When a solid dissolves, the rate is proportional to its surface and to the difference between the saturation-concentration and that at the given moment. At the boundary between the phases saturation exists, so that the rate of solution depends on the diffusion velocity. When a chemical action is superposed, Nernst assumes that in most cases the equilibrium in the reaction-layer is adjusted with practically infinite velocity compared with the diffusion process. If the length of the diffusion path and the diffusion coefficients are known, in many cases the velocity may be calculated in absolute measure.

* R. Abegg, 'Archiv f. Wiss. Phot.,' 1899, vol. 1.

† v. Ostwald, 'Lehrbuch,' 2te Auflage, 2te Bd., 2te Fl. 'Chem. Kinetik.'

‡ 'Zeit. f. Phys. Chem.,' 23.

§ M. Wilderman, 'Phil. Mag.,' October, 1902; 'Zeits. Physik. Chem.,' vol. 30, 1890, p. 341.

|| 'Zeit. f. Phys. Chem.,' 47, 1904, p. 56.

Now, the chemical equation for development with ferrous oxalate is probably $\overset{+}{\mathrm{Ag}} + \overset{-}{\mathrm{Fe}}\,(\mathrm{C_2\overset{-}{O}_4})_2 = \underset{\text{(met.)}}{\mathrm{Ag}} + \overset{-}{\mathrm{Fe}}\,(\mathrm{C_2\overset{-}{O}_4})_2$, *i.e.*, one silver ion is converted into metallic silver. The velocity equation will then be $dx/dt = \mathrm{K}C_{\overset{+}{\mathrm{Ag}}}\,C_{\overset{--}{\mathrm{FeOx}}}$.

C_{Ag} may be reckoned as constant on the above view of the instantaneous adjustment of the equilibrium, as solid AgBr is present. If we assume a layer of constant thickness, δ, in which diffusion takes place, then there will diffuse into the reaction-layer $\mathrm{S}\,\frac{\Delta}{\delta}\,(a-x)\;dt$ of reducer in the time dt, where Δ is the diffusion coefficient of the reducer, a its initial concentration, and x equivalents of AgBr have been reduced. If x be very small compared with a, the total concentration, this becomes $\mathrm{S}\,\frac{\Delta}{\delta}\,a.dt$, and the velocity of development is given by $dx/dt = \mathrm{KS}$, where S is the surface of the solid phase, and $\mathrm{K} = \Delta.a/\delta$. Now the existence of a maximum and fixed quantity of developable AgBr is proven by the experiments detailed above. We shall distinguish the amount of this by $(\mathrm{Ag\overline{Br}})$ and in the course of the reaction it varies from $(\mathrm{Ag\overline{Br}})$ to O. The surface S, therefore, also varies from $\phi\,(\mathrm{Ag\overline{Br}})$ to O. Now, the microscopic examination of the photo-film shows that it consists of a number of very fine AgBr grains embedded in gelatine. This, and the fact that the emulsion absorbs light, according to the law $\mathrm{I}/\mathrm{I}_0 = e^{-m}$ * where m is the mass of haloid, allow us to substitute for $\mathrm{S} = \phi\,(\mathrm{Ag\overline{Br}})$, $\mathrm{S} = p\,(\mathrm{Ag\overline{Br}})$, *i.e.*, the surface is directly proportional to the mass of AgBr at any time, and therefore to its optical density. The optical density D_0 of the latent image $(\mathrm{Ag\overline{Br}})$ must equal D_∞, the density reached on ultimate development, while, obviously, the density of the $(\mathrm{Ag\overline{Br}})$ at any time, t, equals $\mathrm{D}_\infty - \mathrm{D}$, where D is the density of reduced silver at the time, t. Hence $d\mathrm{D}/dt = \mathrm{KS} = \mathrm{K}\,(\mathrm{D}_\infty - \mathrm{D})$, which gives on integration

$$\frac{1}{t}\log\frac{\mathrm{D}_\infty}{\mathrm{D}_\infty - \mathrm{D}} = \mathrm{K}.$$

If this formula be written $\mathrm{D} = \mathrm{D}_\infty(1 - e^{-\mathrm{K}t})$, it will be seen to be the same as Hurter and Driffield's, when $e^{-\mathrm{K}} = a$, but it has been obtained on quite general grounds, free from hypothesis, as to the nature or distribution of the developable haloid.

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* A fine-grained heterogeneity may be treated formally as a solution, *cf.* Bredig, "Anorganische Fermente," Leipzig, and Bodenstein, 'Zeit. f. Physik. Chem.,' 49, p. 42, 1904.

Tested experimentally, the first series gave a decreasing value for K. It was found that this was due to the accumulation of bromide, which lowered the velocity. This was avoided by adding excess of free bromide in such quantity that the amount due to development was negligible.

The following series give some of the results :—

Table IV.

$$K = \frac{1}{t}\log_{10}\frac{D_\infty}{D_\infty - D}.$$

Series I.

Time.	Density.	K.
5·0 mins.	0·294	0·0144
10·0 ,,	0·742	0·0212
15·0 ,,	0·973	0·0205
20·0 ,,	1·178	0·0207
25·0 ,,	1·276	0·0190
30·0 ,,	1·448	0·0203
40·0 ,,	1·547	0·0180
95·0 ,,	1·828	0·0195
135·0 ,,	1·899	0·0199
∞	1·919	

Mean... K = 0·01995.

Series II.

Time.	Density.	K.
5·0 mins.	0·370	0·0182
10·0 ,,	0·683	0·0186
15·0 ,,	0·999	0·0206
20·0 ,,	1·203	0·0206
25·0 ,,	1·270	0·0181
30·0 ,,	1·479	0·0203.
160·0 ,,	1·962	
∞	1·962	

Mean... K = 0·0194.

Series III.

Time.	Density.	K.
5·0 mins.	0·311	0·0149
10·0 ,,	0·838	0·0229
15·0 ,,	1·000	0·0193
20·0 ,,	1·266	0·0208
25·0 ,,	1·401	0·0199
∞	2·053	

Mean... K = 0·01992.

Series IV.

Time.	Density.	K.
5·0 mins.	0·283	0·0190
10·0 ,,	0·547	0·0208
15·0 ,,	0·759	0·0217
20·5 ,,	0·919	0·0214
25·0 ,,	0·990	0·0203
30·0 ,,	1·114	0·0217
45·5 ,,	1·276	0·0209
∞	1·437	

Mean... K = 0·0208.

Total mean of four series ...... K = 0·0203

The developer was—

$$\left.\begin{array}{rl} 4{\cdot}00 \text{ c.c.} & \text{FeSO}_4 \text{ mol.} \\ 2{\cdot}00 \;\;,, & \text{KBr, N/10} \\ 40{\cdot}00 \;\;,, & \text{K}_2\text{C}_2\text{O}_4 \text{ mol.} \end{array}\right\} \begin{array}{l} \text{Fe} = \text{N/25.} \\ \text{Br} = \text{N/500.} \end{array}$$

To 100·0 c.c. with H_2O.

Another batch of the same emulsion gave—

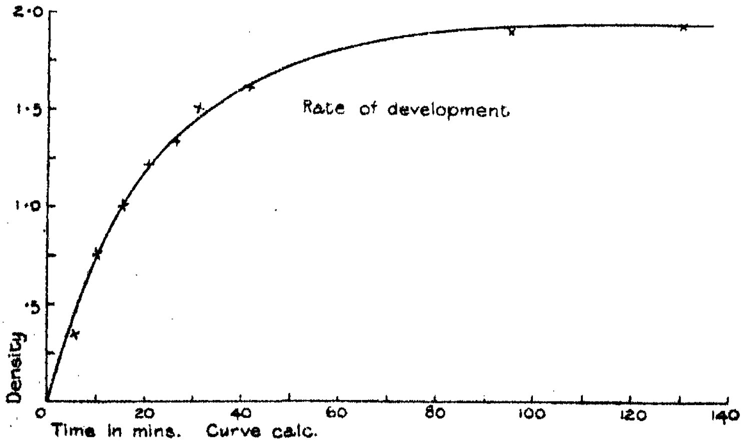
Series I......	K = 0·0191,	Series III......	0·0217,
„ II......	K = 0·0201,	„ IV......	0·0204.

Total mean .... 0·0204,
Total mean of four series... K = 0·0203.

The following table and curve show that the expression is satisfactory over a wide range of development, considering the experimental difficulties. All the series, D_1, D_2, and D_3, were reduced by common proportion to the same value :—

Table V.—Curve for N/500 $\overline{\text{Br}}$ and N/25 Ferrous Oxalate.

Time in mins.	D_1.	D_2.	D_3.	D obs.	D calc.
5·0	0·330	0·303	0·373	0·335	0·410
10·0	0·773	0·815	0·697	0·762	0·736
15·0	1·018	0·975	1·020	1·003	0·995
20·0	1·227	1·232	1·228	1·229	1·201
25·0	1·330	1·365	1·296	1·330	1·364
30·0	1·510		1·510	1·510	1·495
40·0	1·610			1·610	1·681
95·0	1·904			1·904	1·960
135·0	1·970			1·970	1·980
∞	2·000	2·000		2·000	2·000



It appears that generally the value of K is constant for a standard emulsion freshly coated. Variations, however, may be caused by different emulsification, and the value varies with different plates.

Thus

Wratten ordinary .... $K = 0{\cdot}0203$
Barnet ordinary .... $K = 0{\cdot}0260$ $(0{\cdot}0249 - 0{\cdot}0254)$

For occasions of space the mean value of K with the extremes are given, except where it seems desirable to show that the course of the reaction is unchanged.

Influence of Concentration on the Velocity.—The constant as developed above contains implicitly C_{Fe}, the total concentration of the iron; it should, therefore, be proportional to this experimentally.

Table VI.

$C_{\text{Ferrous oxalate}}$.	K found.
N/12·5	0·4011
N/12·5	0·4061
N/25	0·203
N/50	0·100
N/50	0·102

$\bar{\mathrm{Br}} = \mathrm{N}/500$

The values for N/12·5 showed some tendency to decrease; this is probably due to the rapid accumulation of bromide and other reaction products, which do not diffuse rapidly, and so influence the velocity by remaining in the reaction layer, a fact which is one of the main causes of divergencies and difficulties in heterogeneous reactions.* A more stringent proof of the proportionality is given later.

On the diffusion theory of the development velocity, this proportionality is simply the expression of the fact that the amount of reducer diffusing into the reaction layer is proportional to the concentration (*vide* p. 457). Nernst† has pointed out that on this theory it is not admissible to draw conclusions as to the order of the reaction in heterogeneous systems, so that the otherwise probable theory, that the reaction is mono-molecular with respect to iron, cannot be regarded as strictly proven by this.

Influence of Bromide on the Velocity.—It is well known to photographers that bromide considerably influences the rate of development, for which reason it is used as a restrainer. The influence of bromide must be due to its effect on the purely chemical reaction

$$\overset{+}{\mathrm{Ag}} + \bar{\mathrm{R}} = \underset{(\text{met.})}{\mathrm{Ag}} + \bar{\mathrm{R}}.$$

The effect on the expression $K = \frac{1}{t}\log\frac{D_\infty}{D_\infty - D}$ was studied.

It was found that the values of K for low values of t increased till a fairly constant maximum period was reached. This initial induction was already noticeable in N/500 bromide, and increased as the concentration of the bromide increased. Further, it was modified by the value of D_∞, *i.e.*, of $(\overline{\mathrm{AgBr}})$, being shorter for higher values of this. Values of K were obtained from "maximum" period.

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* Ostwald, 'Lehrbuch,' 2te Auflage, 2te Bd., 'Chem. Kinetik.'

† W. Nernst, 'Theoretische Chemie,' 4te Auflage, p. 573.

Results.

Developer, N/25 Ferrous oxalate.
N/1000 KBr.

I. *a.* K = 0·0280 (0·023—0·031). Increase due to fog.
b. K = 0·0280 (0·030—0·026).

II. KBr = N/100.	III. KBr = N/50.
a. K = 0·0145 (0·0142—0·017).	*a.* K = 0·0123 (0·0110—0·0147).
b. K = 0·0142 (0·0169—0·0137).	*b.* K = 0·0113 (0·010—0·0130).

And with N/12·5 Ferrous oxalate—

Series I. KBr = N/50.

a. K = 0·0181 (0·0166—0·0203). *b.* K = 0·0182 (0·0195—0·0176).

Tabulating results we get—

Developer N/12·5 Ferrous oxalate.

Concentration of Br.	Velocity constant.
0·002 N	0·0404
0·020 N	0·0181

And for the lower concentration N/25 Ferrous oxalate.

Concentration of KBr.	K.	K × log Br.
0·001 N	0·0280	0·0280
0·002 N	0·0203	0·0265
0·010 N	0·0143	0·0285
0·020 N	0·0118	0·0274
		C = 0·0276

It will be seen that the results obtained with bromide are fairly represented by the simple empirical formula $K \times \log_{10} \overline{Br}$ = constant, *i.e.*, as the bromide is increased in geometrical progression, the velocity diminishes in arithmetical.

We may discuss here the theoretical grounds from which the behaviour of bromide might be deduced.

It has been suggested that the action of bromide is due to the reversal of development, silver bromide being re-formed and development retarded,* but the writers found that the addition of small quantities of ferric oxalate, the other reaction-product, had no effect comparable with that due to equimolecular quantities of bromide. Only with very large concentrations of ferric oxalate (above N/25) was an effect perceived. Bromide is therefore shown by this method of "isolation" to have an effect *per se*. A more probable theory is that bromide acts by lowering the concentration of the silver ions in accordance with the reversible ionic equilibrium

$$\overset{+}{\mathrm{Ag}} + \overset{-}{\mathrm{Br}} \rightleftarrows \underset{\text{(solut.)}}{\mathrm{AgBr}} \rightleftarrows \underset{\text{(solid)}}{\mathrm{AgBr}},$$

when we have $C_{Ag} . C_{Br} = \text{constant}$.

Now, the chemical equation gives

$$dD/dt = K . C_{Ag} . C$$

for the reaction velocity, and in consequence, the velocity should be inversely as the concentration of the bromide ions. That it has a smaller effect than this confirms the view that the reaction-velocity is chiefly determined by the diffusion equation. Nevertheless, bromide may so slow the chemical reaction that its velocity begins to affect that of the total reaction.

We may further notice, as was remarked above, that the expression $\frac{1}{t} \log \frac{D_\infty}{D_\infty - D} = K$ does not hold over so wide a range when bromide is introduced, but that the values of K rise at first, and then reach a fairly constant period, the induction-period apparently depending both on the concentration of the bromide and on the value of D_∞. The phenomena observed are similar to those in "graded" reactions taking place in homogeneous systems.† These initial disturbances are intimately connected with the disturbance of the density ratios by bromide. In order to investigate the action more fully, a series of exposures on the same plate, thus giving different values of D_∞, were obtained by means of the previously described sensitometer; the results of this work will be noted later, with an elaborated theory of the mechanism of development.

Age of Plate.—In the course of this work, it was found that the velocity of development depends largely on the age of the plate, diminishing with keeping. This change is accelerated by heat and atmospheric conditions. This was discovered when plates of Batch I were used a considerable time after making, and gave quite divergent velocities according as they had been kept. The phenomenon, while the cause was still unsuspected, caused much trouble. The following tables exhibit the divergencies obtained:—

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* Hurter and Driffield, 'Phot. Journal,' 1898; Luther, 'Chemische Vorgänge in der Photographie,' 1900.

† J. Walker, 'Proc. Roy. Soc., Edinburgh,' December, 1897.

Table VII.—Developer Fe = N/25, KBr = N/500, K = ·0203.*

Time.	Density.	$K = \frac{1}{t}\log\frac{D_\infty}{D_\infty - D}$.
15·0 mins.	0·259	0·0048
20·0 ,,	0·452	0·0066
30·0 ,,	0·643	0·0068
40·0 ,,	0·816	0·0070
50·0 ,,	0·960	0·0071
60·0 ,,	1·042	0·0068
70·0 ,,	1·089	0·0062
80·0 ,,	1·214	0·0067
90·0 ,,	1·302	0·0069
100·0 ,,	1·333	0·0065
120·0 ,,	1·423	0·0064
12 hrs.	1·713	
14 ,,	1·712	

Mean, K = ·0067, *i.e.*, a reduction to one-third of its former value. This was for an opened box kept in laboratory cupboard.

Table VIII.

Developer Fe = N/25. $\overline{\text{Br}}$ = N/500.

Time.	Density.	K.
10·0 mins.	0·226	0·0062
15·0 ,,	0·575	0·0118
25·0 ,,	0·713	0·0094
30·0 ,,	0·835	0·0097
40·0 ,,	1·041	0·0102
50·0 ,,	1·185	0·0102
60·0 ,,	1·284	0·0101
70·0 ,,	1·411	0·0108
80·0 ,,	1·432	0·0099
190·0 ,,	1·666	
6 hrs.	1·708	

K = 0·01004

Table VIII*a*.

Fe = N/25. $\overline{\text{Br}}$ = N/1000.

Time.	Density.	K.
10·0 mins.	0·552	0·0174
16·5 ,,	0·744	0·0185
20·0 ,,	0·891	0·0166
25·0 ,,	0·900	0·0136
30·0 ,,	1·040	0·0141
40·0 ,,	1·277	0·0157
50·0 ,,	1·375	0·0151
60·0 ,,	1·403	0·0134
175·0 ,,	1·646	
∞	1·669	

K = 0·01555

The values obtained six months before were

N/500 $\overline{\text{Br}}$. K = 0·0203. N/1000. K = 0·0280,

so that in this case the speed has been about halved. This was for a sealed box kept in laboratory cupboard.

Further, for an opened box kept in college locker:—

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* See table, pp. 458—459.

Table IX.

N/500 KBr. K = 0·0203.

Time.	Density.	K.
10·0 mins.	0·513	0·0156
15·0 „	0·809	0·0195
20·0 „	1·002	0·0200
26·0 „	1·115	0·0185
30·0 „	1·174	0·0180
45·0 „	1·418	0·0184
60·0 „	1·560	0·0190
190·0 „	1·664	
3 hrs.	1·664	

Mean… K′ = 0·0189.

Table IX*a*.

N/200 KBr. K = 0·0170.

Time.	Density.	K.
10·0 mins.	0·549	0·0149
15·0 „	0·835	0·0168
20·0 „	0·961	0·0163
25·0 „	1·119	0·0155
30·0 „	1·274	0·0161
40·0 „	1·461	0·0160
46·0 „	1·562	0·0164
60·0 „	1·688	0·0162
∞	1·895	

Mean… K′ = 0·01603.

In this case a reduction of only 5 per cent. in the velocity has taken place.

These measurements show that the rate at which a plate develops is diminished with time of keeping. Apparently a slow irreversible change takes place in the film, which is accelerated by heat and presence of gases, etc. If we consider the expression for the velocity $K = \frac{\Delta}{\delta} . a .$, it seems probable that the alteration is due to an effect on Δ, the diffusivity coefficient. It is quite different from that produced by so-called "hardening" agents, which do not affect the development velocity.

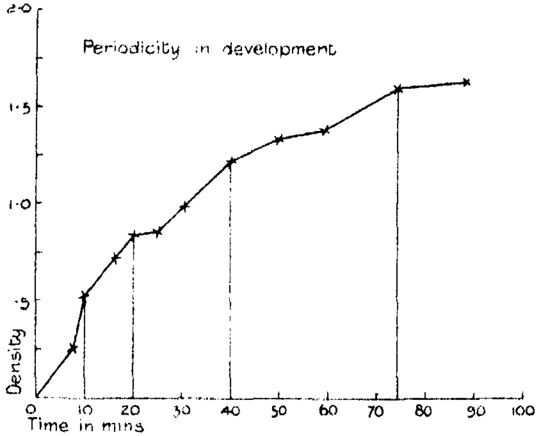
Only the absolute value of the velocity, and not the velocity-function, is altered.

The Diffusion Path, δ.—In his work on heterogeneous reactions, Bruner measured the thickness of the diffusion layer by electro-chemical reactions, and found, for example, for rate of solution in water of benzoic acid, 0·03 mm. In general, the layer was of this order, but was lessened as the rate of stirring increased.

In the photo film the diffusion path must be equal to the depth of the latent image plus a small layer on the gelatine surface. The former is not alterable by stirring, and the subsequent microscopic measurements show that it is of about the same order as Bruner found, viz., about 0·02 to 0·03 mm. The outer layer is alterable by rotation, but is probably not very large, as increasing the rotation had but a slight effect on the velocity. Unfortunately, very high velocities of stirring increased the fog materially, and also produced uneven marking. A rate of about 30 revolutions per minute was found to ensure homogeneity of the solution on the bounding surface.

It should be noticed that the whole mass and surface of the developable image in the case of development lie in the short diffusion layer in the gelatine. How far this modifies the Nernst theory for the reaction-velocity will be considered later.

A slight periodicity in the rate of development was sometimes noted, see curve*.



Note on Fog.—It is usual in density measurements to subtract the so called "fog" from the total density. This is the density due to inherent fog in the plate, extraneous light, etc. Usually a separate reading is made of the so-called fog strip, but, owing to the differential nature of our instrument, the "fog" reading was automatically subtracted, and taken from the same portion of emulsion as the exposure.

But the formula $\frac{1}{t}\log\frac{D_\infty}{D_\infty - D} = K$ shows that there is a theoretical error in assuming the fog in the unexposed strip is equal to that in the exposed strip.

For let $A + B = C$ be total mass AgBr,

where A = AgBr changed by light, B = AgBr unchanged.

Then rate of fogging $= (dD/dt)\, C = K\,(A + B)$ in fog strip, and equals $(dD/dt)\, B = KB$ in exposed film.

Obviously, fog increases faster in unexposed film than in the exposed; it is desirable, therefore, for photo-chemical investigations, to have an emulsion which does not give fog-density higher than 0·15 to 0·2, even on infinite development, and in most of this work this was fulfilled.

Law of Constant Density Ratios.—Another deduction from the development formula is the law of constant density ratios. If a series of increasing exposures are given to a plate, as every density increases proportionately, the ratio of the densities due to any two exposures is constant, and independent of the time of development.

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* *Cf.* Ostwald, 'Vorles. über Naturphil.,' Leipzig, 1902, pp. 274, 315, 362, 'Zeit. Phys. Chem.,' 35, p. 33, 1900. G. Bredig u. Weinmayer, 'Z. f. p. Chem.,' 42, p. 600, "Periodic Contact Analysis."

Hurter and Driffield showed that if a geometrically increasing series of exposures be given to a plate over a certain range, the density increased arithmetically. Over this period of "correct exposure" the following equation holds :—$D = \gamma \log E/i$, where E is the exposure, i is a characteristic constant of the plate, termed the inertia, and γ is a constant depending upon the development, and called the development factor. The magnitudes i and γ are obtained graphically as follows: the densities due to nine successive exposures are plotted as ordinates, and the logarithms of the corresponding exposures as abscissæ. A curve is obtained which, for a certain period, is practically a straight line. The point where this cuts the exposure axis gives $\log i$, and if θ be the angle of inclination, $\gamma = \tan \theta$. Analytically, the value of γ may be deduced as follows: for two exposures, E_1 and E_2, we obtain the densities D_1 and D_2, the equations being

$$D_1 = \gamma \log E_1/i, \; D_2 = \gamma \log E_2/i,$$

eliminating i,

$$\gamma = \frac{D_2 - D_1}{\log E_2 - \log E_1} = \frac{\Delta D}{\Delta \log E};\text{*}$$

γ is therefore independent of the absolute exposure, and only dependent on the E_2/E_1 which is fixed by the sector wheel.†

In order to test the constancy of the density ratios, two plates were exposed simultaneously in the sensitometer to avoid errors due to light inconstancy, and developed for different times. The values of γ were obtained from the curves in the graphic manner described. Each plate was allowed 100 c.c. of developer.

$FeSo_4$ Mol. 8·0 c.c. + $K_2C_2O_4$ Mol. to 100 c.c.

The logarithms of the exposures are given on an arbitrary scale, putting $\log E_9 = 1{\cdot}0$, as the absolute value is unimportant. A typical table is given below :—

Table X.—T_1 = 2 mins., T_2 = 6 mins.

No.	Log E.	Density T_1.	Density T_2.	Ratio D_1/D_2.
1	3·30	—	—	—
2	3·012	0·876	2·563	2·935
3	2·72	0·759	2·230	2·900
4	2·42	0·685	1·995	2·920
5	2·14	0·499	1·491	2·983
6	1·80	0·332	1·096	3·330
7	1·575	0·234	0·716	3·050
8	1·360	0·128	0·329	2·680
			Mean ...	2·957

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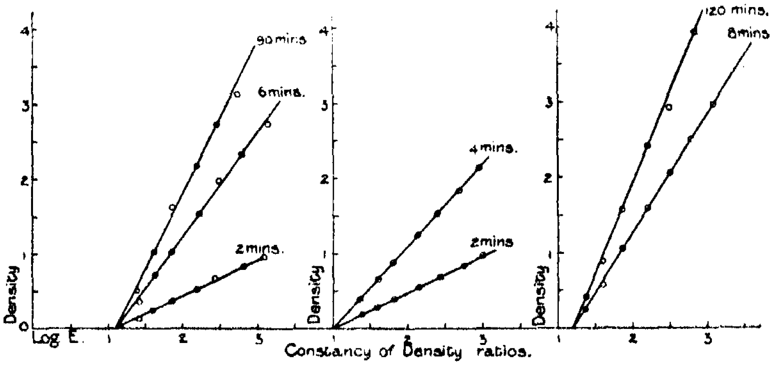
* Or $D = \gamma \frac{\log E}{i}$, hence $\gamma = \frac{dD}{d \log E}$.

† For calibration of sector-wheel v. *loc. cit.*, p. 2.

Other results abbreviated :—

Series II ...	R = 1·465.	Mean dev. = ∓0·04.	T_1 = 6 mins.
			T_2 = 120 ,,
,, III ...	R = 2·21.	,, = ∓0·04.	T_1 = 2 ,,
			T_2 = 4 ,,
,, IV ...	R = 1·49.	,, = ∓0·05.	T_1 = 8 ,,
			T_2 = 120 ,,
,, V ...	R = 1·353.	,, = ∓0·032.	T_1 = 5 ,,
			T_2 = 10 ,,
,, VI ...	R = 1·48.	,, = ∓0·05.	T_1 = 10 ,,
			T_2 = 120 ,,

Range of exposure	1—250.
,, development	2 mins. to 2 hrs.



Constancy of Density ratios.

The ratios of densities due to different exposures are unchanged by time of development in a non-bromided developer.

These tables and the curves show that for variations in the time of development from 2 minutes the density ratios and the values of *i* are unaffected. Every density grows proportionately with the time, a fact which finds its rational explanation in the theory of development proposed.

For the straight line portion of exposure the equation $D = \gamma(\log E - \log i)$ holds, and for a single density the expression in brackets is a constant. The development factor, γ, is, therefore, strictly proportional to D, and as

$$D = D_{\infty}(1 - e^{-Kt}),$$

so
$$\gamma = \gamma_{\infty}(1 - e^{-Kt}),$$

where
$$\gamma = \gamma \text{ at time } t,$$

$$\gamma_{\infty} = \gamma \text{ infinite dev.},$$

which gives the relation between γ and the time of development.

The following tables show the validity of the expression for different batches of plates :—

Table XI.

Time.	Development factor γ	$\frac{1}{t}\log_{10}\frac{\gamma_\infty}{\gamma_\infty - \gamma}$.
2·0 mins.	0·50	0·0460
2·5 „	0·73	0·0562
4·0 „	1·08	0·0572
5·0 „	1·33	0·0608
6·0 „	1·47	0·0578
8·0 „	1·77	0·0602
10·0 „	1·91	0·0541
15·0 „	2·17	0·0480
∞	2·67	
	Mean ...	0·0550

Table XII.

Time.	γ.	$K = \frac{1}{t}\log\frac{\gamma_\infty}{\gamma_\infty - \gamma}$.
2·0 mins.	0·684	0·0495
2·5 „	0·840	0·0500
4·0 „	1·23	0·0500
5·0 „	1·63	0·0470
8·0 „	1·90	0·0470
∞	3·40	
	Mean ...	K = 0·0487

This shows that both γ_∞ and K vary for different batches; for the same developer, γ_∞ and K are the characteristic development constants of the emulsion.

The factor γ is of considerable importance in practical photography, as it measures the gradation or degree of contrast in a negative.

Influence of Concentration on γ.—As might be expected, this is simply, the time taken to reach a given factor is inversely as the concentration of the ferrous oxalate.

Thus for N/12·5 and N/25 ferrous oxalate—

N/25 ...... 5·0 mins. ...... $\gamma = 0{\cdot}73$
N/12·5 ... 2·5 „ ...... $\gamma = 0{\cdot}72$
N/25 ...... 5·0 „ ...... $\gamma = 1{\cdot}54$
N/12·5 ...... 10·0 „ ...... $\gamma = 1{\cdot}59$

Over the range N/5 to N/40—

(A) N/5 ...... 1·5 mins.
(B) N/10 ...... 3·0 „
(C) N/20 ...... 6·0 mins.
(D) N/40 ...... 12·0 „

Table XIII.

E.	Log E.	D_A.	D_B.	D_C.	D_D.	Mean D.
304·5	2·48	—	1·358	1·440	1·446	1·414
154·8	2·19	1·302	1·248	1·278	1·270	1·274
78·0	1·89	1·094	1·114	1·104	1·120	1·108
40·6	1·61	0·892	0·892	0·902	0·850	0·884
18·8	1·26	0·604	0·688	0·676	0·608	0·644
11·1	1·05	0·422	0·436	0·428	0·358	0·414
6·72	0·88	—	0·244	—	—	0·244

The velocity of development is proportional to the concentration of the ferrous oxalate.

The magnitude γ_∞, *i.e.*, the limiting γ of the plate, is of great importance. It expresses numerically the ultimate density-giving powers of plates, and gives a numerical measure of the quality that has hitherto been expressed by such phrases as "contrasty plates," soft plates, "flaue platten," and so forth. γ_∞ is proportional to the photometric constant of the reduced silver, and so varies slightly with the developer, but more so with the emulsification of the haloid.

The practical estimation of γ_∞ and D_∞ is in many cases beset with much experimental difficulty. If γ_∞ is very high, the resultant densities are hard to measure, while many commercial plates, especially rapid ones, give much fog on prolonged development. Since the equilibrium is only theoretically reached after infinite time, only a close approximation is reached by very long development. The method given by Ostwald* for evaluating the end-result was employed to check the results.

The following method of obtaining γ_∞ and K from simultaneous values of γ and t was pointed out by Dr. L. N. G. Filon:—

Writing the equation $\frac{1}{t}\log_e \frac{\gamma_\infty}{\gamma_\infty - \gamma} = \mathrm{K}$ in the form $\gamma = \gamma_\infty(1 - e^{-\mathrm{K}t})$, and taking γ_1 and γ_2 so that $t_2 = 2t_1$, we get

$$\gamma_1 = \gamma_\infty(1 - e^{-\mathrm{K}t_1}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (a),$$

$$\gamma_2 = \gamma_\infty(1 - e^{-\mathrm{K}t_2}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (b),$$

putting $e^{-\mathrm{K}t_1} = x$ we have from (*a*) and (*b*)

$$\frac{\gamma_1}{\gamma_2} = \frac{1 - x}{(1 - x^2)} = \frac{1}{1 + x} = \frac{1}{1 + e^{-\mathrm{K}t_1}},$$

$$\therefore \quad \frac{\gamma_2 - \gamma_1}{\gamma_1} = e^{-\mathrm{K}t_1}, \qquad \frac{\gamma_1}{\gamma_2 - \gamma_1} = e^{\mathrm{K}t},$$

and

$$\frac{1}{t}\log_e \frac{\gamma_1}{\gamma_2 - \gamma_1} = \mathrm{K},$$

---

* 'Lehrbuch,' 2te Auflage, 2 Th., 2 Bd., p. 210.

which gives K, whence γ_∞ may be obtained by substitution; but it must be noticed that the expression only holds when $\gamma_2/\gamma_1 = < 0{\cdot}8$ approximately, *i.e.*, when the tangential part of the curve is past.

Comparison of Developers.—By means of the γ formulæ the relative efficiencies for different developers can be compared. The following results give the comparison for ferrous oxalate, fluoride, and citrate:—

Ferrous Fluoride.—The use of this salt was suggested by Peters' work on the reduction potential of ferrous salts. Luther explains the fact that ordinary ferrous salts—$Fe''R$—as $FeSO_4$ do not develop as due to the reversal of the reaction by ferric ions. But Peters has shown that the E.M.F. of a ferrous chain is very much increased by the addition of a soluble fluoride, owing to the fact that $Fe'''Fl_3$ is but slightly dissociated, and further that a complex ferrid-fluoridion is formed, both causes tending to remove ferric ions. We found that an N/10 solution of $FeSO_4$ in excess of KF developed but slowly. Prolonged development removed the film from the plate, so that celluloid films had to be used.

The developer was made by mixing $FeSO_4$ and NaF solutions, as the sodium double salt seems more soluble than the potassium one. The solutions were nearly colourless.

Table XIV.—Ferrous Oxalate, N/10.

Temp. 13° C.

Time.	γ.	$\frac{1}{t}\log_{10}\frac{\gamma_\infty}{\gamma_\infty-\gamma}$.
3·0 mins.	0·64	0·056
6·0 „	1·13	0·060
8·0 „	1·39	0·064
∞	2·00	——
		K = 0·060

Temp. 20° C.

Time.	γ.	$\frac{1}{t}\log_{10}\frac{\gamma_\infty}{\gamma_\infty-\gamma}$.
2·0 mins.	0·49	0·062
4·0 „	1·01	0·076
7·0 „	1·35	0·071
8·0 „	1·49	0·074
∞	2·00	——
		K = 0·071

$\gamma_\infty = 2{\cdot}00$, mean value found by Filon's expression.

The experiments with ferrous fluoride showed that the law of the constancy of inertia with time of development held here. For brevity, only the γ values are given.

Table XV.—Ferrous Fluoride, N/10.

Temp. 13° C.

Time.	γ.	$\frac{1}{t}\log_{10}\frac{\gamma_\infty}{\gamma_\infty-\gamma}$.
45·0 mins.	0·50	0·0028
90·0 ,,	1·00	0·0033
135·0 ,,	1·35	0·0036
280·0 ,,	1·72	0·00303
∞	2·00	———
		K = 0·0032

Temp. 20° C.

Time.	γ.	$\frac{1}{t}\log_{10}\frac{\gamma_\infty}{\gamma_\infty-\gamma}$.
15·0 mins.	0·204	0·0030
60·0 ,,	0·895	0·0043
90·0 ,,	1·22	0·0045
120·0 ,,	1·36	0·0041
∞	2·00	———
		K = 0·0043

Hence, comparing results,

Temp.	K Ferrous oxalate.	Ferrous fluoride.	Ratio.
13° C.	0·060	0·0032	18·7
20° C.	0·071	0·0043	16·5

This indicates that ferrous fluoride has a somewhat higher temperature-coefficient than ferrous oxalate.

Ferrous Citrate.—This is a good developer for chloride plates, but develops silver bromide very slowly. For the plates employed $\gamma_\infty = 3·40$, and K for ferrous oxalate at 20° C. = 0·0487.

It was found that here also the density ratios and the inertia were independent of the time of development. For the velocity at 20° C.—

Table XVI.—Ferrous Citrate, N/10.

Time.	γ.	$\frac{1}{t}\log_{10}\frac{\gamma_\infty}{\gamma_\infty-\gamma}$.
60·0 mins.	0·474	0·0011
120·0 ,,	0·720	0·0009
240·0 ,,	1·40	0·00096
∞	3·40	———
		K = 0·0010

Whence for table of relative efficiencies at 20° C.—

Developer.	**Efficiency = K**
Ferrous citrate	**1·00**
Ferrous fluoride	**2·95**
Ferrous oxalate..................	**48·7**

On the Theory of Development.—In the ferrous fluoride developer the reducing agent seems most probably the ferrous ion, $\overset{++}{\mathrm{Fe}}$, the concentration of which is extremely high. With ferrous citrate, a complex ferro-citratanion. Now, on the diffusion theory the great difference in velocity observed is difficult to explain; in particular, the mobile ferrous ion should have proved the most efficient reducer. Possibly we still have to do with the influence of free ferric ions on the reduction velocity, although their original concentration in the ferrous fluoride solutions was extremely small, while those formed by the reaction $\overset{++}{\mathrm{Fe}} + \overset{+}{\mathrm{Ag}} \rightleftarrows \overset{+++}{\mathrm{Fe}} + \mathrm{Ag}$ (metal), should be immediately removed by the ionic equilibria

$$\overset{+++}{\mathrm{Fe}} + 3\overset{-}{\mathrm{F}} \rightleftarrows \mathrm{FeF_3}$$

and

$$\overset{+++}{\mathrm{Fe}} + 6\overset{-}{\mathrm{F}} \rightleftarrows \overset{---}{\mathrm{FeF_6}}.$$

However, the action of bromides shows that the actual chemical reaction can, under certain circumstances, influence the total reaction velocity. Although, in general, ionic reactions, such as we must conceive development to be, occur with practically immeasurable velocity, yet it is possible to follow some in which the ionic concentration is very low.* In the development of silver bromide, the concentration cannot pass the solubility product of AgBr, so that the maximum concentration of silver ions is very low. Further, the unknown nature and influence on the reaction of the so-called latent image have not been taken into account.

Bodenstein,† in a criticism of the Nernst-Bruner theory, has indicated the presence of a high temperature coefficient as a criterion for distinguishing whether the speed of reactions in heterogeneous systems is conditioned by the diffusion process or the chemical reaction. A study of the temperature-influence, of the influence of soluble bromides, the reversibility of the reaction, and of the microscopy of development and exposure has been made, in continuance of the present work, as well as experiments on the nature and destruction of the "latent image," and it is hoped to publish these shortly.

The work given here shows that development can be studied quantitatively, and brings it in line with general physico-chemical.

Summary of Results.—(1) An accurate quantitative method of attacking photographic questions is described, and it is shown that if T be the optical transparency of the silver deposited in photographic processes, the D = − log T is accurately proportional to the mass of silver.

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* *Cf.* Donnan and Le Rossignol, "Velocity of Reaction between Potassium Ferricyanide and Iodide in Neutral Solution," 'J. C. S. Trans.,' p. 703, 1903.

† M. Bodenstein, 'Zeit. f. Physik. Chem.,' 49, H. 1, p. 42, 1904.

(2) From considerations of the growth of the density during development, and of the theory of heterogeneous reactions, the equation $\frac{1}{t}\log\frac{D_\infty}{D_\infty - D} = K$, a constant, was shown to represent the reaction; this was experimentally confirmed. It is considered that the velocity of development mainly depends upon the rate of diffusion to the affected haloid. In agreement with this (*a*), the velocity as measured by the constant above, is directly proportional to the concentration of the reducer; (*b*) is affected by the age and condition of the plate; (*c*) is reduced by the addition of soluble bromides, but not in the proportion which would occur if the velocity of the chemical reaction $\overset{+}{Ag} + \overset{--}{R} = Ag\ (met.) + \overset{--}{R}$ alone were measured.

(3) The law of constant density-ratios due to varying exposures, deduced from the above theory, is experimentally confirmed.

(4) It is shown that the development-factor γ in the sensitometry equation $D = \gamma \log E/i$ is governed by the same laws as a single density. Methods for calculating and controlling γ are given, by means of the equation $\frac{1}{t}\log\frac{\gamma_\infty}{\gamma_\infty - \gamma} = K$.

(5) By means of this expression the velocities with ferrous oxalate, fluoride, and citrate were compared, the relative values of K being in N/10 concentration 0·0487, 0·003, 0·001; the anomalies here and the theory of development are discussed.

In conclusion, it is our pleasant duty to express our thanks to Professor Sir William Ramsay, F.R.S., for continual interest and advice throughout the research, and also to Dr. F. G. Donnan, and to Dr. M. W. Travers, F.R.S., for much advice and sympathy.

"Polarised Röntgen Radiation." By CHARLES G. BARKLA, D.Sc., B.A., King's College, Cambridge, Oliver Lodge Fellow, University of Liverpool. Communicated by Professor J. J. THOMSON, F.R.S. Received January 21,—Read February 16, 1905.

(Abstract.)

Experiments on secondary radiation from gases and light solids subject to X-rays showed that the character of this radiation differs only very slightly from that of the radiation producing it, and that the energy of this radiation is proportional merely to the quantity of matter through which a beam of Röntgen radiation of definite intensity passes, being independent of the kind of matter.

These results, and the agreement between the energy experimentally determined and that calculated, led to the conclusion that this radiation is due to what may be called a scattering of primary X-rays by the corpuscles or electrons constituting the molecules of the substance.

On the hypothesis that Röntgen rays consist of a succession of electro-magnetic pulses in the ether, each electron in the medium through which these pulses pass has its motion accelerated by the intense electric fields in these pulses, and consequently is the origin of a secondary radiation, which is most intense in the direction perpendicular to that of acceleration of the electron, and vanishes in the direction of that acceleration. The direction of electric intensity at a point in a secondary pulse is perpendicular to the line joining this point and the origin of the pulse, and is in the plane passing through the direction of acceleration of the electron.

On this theory, a secondary beam whose direction of propagation is perpendicular to that of the primary, will be plane polarised, the direction of electric intensity being parallel to the pulse front in the primary beam. If the primary beam be plane polarised, the secondary radiation from the charged corpuscles or electrons has a maximum intensity in a direction perpendicular to that of electric displacement in the primary beam, and zero intensity in the direction of electric displacement.

The secondary radiation from light substances was too feeble to allow accurate measurement of the intensity of the tertiary radiation.

A consideration of the method of production of primary Röntgen rays in an X-ray tube, however, leads one to expect partial polarisation of the primary beam proceeding from the antikathode in a direction perpendicular to that of propagation of the impinging kathode rays, for there is probably at the antikathode a greater acceleration along the line of propagation of the kathode rays than in a direction at right

angles; consequently in a beam of X-rays proceeding in a direction perpendicular to that of the kathode stream there should be greater electric intensity parallel to the stream than in a direction at right angles.

Such a beam was therefore used as the primary radiation, and the intensity of secondary radiation proceeding in a direction perpendicular to that of propagation of the primary beam from a radiator placed in that beam, was studied by means of electroscopes.

In the final form of apparatus the intensity of secondary radiation was measured in two directions perpendicular to that of propagation of the primary radiation and to each other, while the intensity of the primary beam was measured by a third electroscope.

Using paper, aluminium, or air as the radiator, as the bulb was turned round the axis of the primary beam studied, the intensity of a secondary beam was found to reach a maximum when the direction of the kathode stream was perpendicular to that of propagation of the secondary beam, and a minimum when these two were parallel, one electroscope recording a maximum rate of deflexion when the other recorded a minimum. Many experiments were made which proved the evidence of partial polarisation conclusive.

When heavier metals, such as copper, tin, and lead, which emit a secondary radiation differing considerably in character from the primary producing it, were used as radiators, no variation in intensity of secondary radiation was observed as the bulb was rotated.

This result was not found to be affected by a considerable variation in the penetrating power of the primary radiation.

Experiments were made with several X-ray tubes.

"On the Conversion of Electric Oscillations into Continuous Currents by means of a Vacuum Valve." By J. A. FLEMING, M.A., D.Sc., F.R.S., Professor of Electrical Engineering in University College, London. Received January 24,—Read February 9, 1905.

An electric oscillation being an alternating current of very high frequency, cannot directly affect an ordinary movable coil or movable needle galvanometer.

Appliances generally used for detecting electric waves or electric oscillations are, therefore, in fact, alternating current instruments, and must depend for their action upon some property which is independent of the direction of the current, such as the heating effect or magnetizing force. The coherer used in Hertzian wave research is not metrical, since the action is merely catastrophic or accidental, and bears no very definite relation to the energy of the oscillation which starts it. Even the demagnetising action of electric oscillations, though more definite in operation than the contact action at loose joints, is far from being all that is required for quantitative research. It is obvious it would be an advantage if we could utilise the direct current mirror galvanometer for the detection and measurement of feeble electric oscillations. This can be done if we can discover a medium with perfect unilateral conductivity.

Some time ago, I considered the use of the aluminium-carbon electrolytic cell with this object. It is well known that a cell containing a plate of aluminium and carbon, immersed in some electrolyte which yields oxygen, such as dilute sulphuric acid or an aqueous solution of any caustic alkali, or salt yielding oxygen, has a unilateral conductivity within limits. An electric current under a certain electromotive force can pass through the cell from the carbon to the aluminium, but not in the reverse direction.

This action has been much studied and is the basis of many technical devices, such as the Nodon electric valve.

The electrochemical action by which this unilateral conductivity is produced involves, however, a time element, and after much experimenting I found that it did not operate with high frequency currents. My thoughts then turned to an old observation made by me in 1889, communicated to the Royal Society, amongst other facts, in a Paper in 1889, and also exhibited experimentally at the Royal Institution in 1890.* This was the discovery: that if a carbon filament electric glow lamp contains a pair of carbon filaments or a single filament and a metallic plate sealed into the bulb, the vacuous space between possesses a unilateral conductivity of a particular kind when the carbon filament, or one of the two filaments, is made incandescent. I have quite lately returned to this matter, and have found that this unilateral conductivity exists even with alternating currents of high frequency and is independent of the frequency. Hence, in a suitable form, it seemed possible that such a device would provide us with a means of rectifying electric oscillations and making them measurable on an ordinary galvanometer. The following experiments were, therefore, tried:—

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* See 'Roy. Soc. Proc.,' vol. 47, p. 122, 1890, "On Electric Discharge between Electrodes at different Temperatures in Air and High Vacua," by J. A. Fleming, communicated December 16, 1889; see also 'Proceedings of the Royal Institution,'

Into a glass bulb, made like an incandescent lamp, are sealed in the ordinary way two carbon filaments, or there may be many filaments. On the other hand, one carbon filament may be used and a platinum wire may be sealed into the bulb terminating in a plate or cylinder of platinum, aluminium or other metal surrounding the filament. It is preferable to use a metal plate carried on a platinum wire sealed into the glass bulb, the plate being bent into a cylinder which surrounds both the legs of the carbon loop. The diagrams in fig. 1 show various forms of the arrangement. Diagram *a* shows a bulb with a single carbon filament surrounded by a metal cylinder, *b* shows one with two carbon filaments, and *c* a carbon filament and two insulated metal plates. The ends of the carbon filament which is rendered incandescent are marked + and − and the terminal of the other electrode of the valve is marked *t*. The bulb must be highly exhausted to about the pressure usual in the case of carbon filament incandescent lamps, and the metal cylinder or plate must be freed from occluded air.

Suppose that we employ such a bulb containing one carbon filament surrounded by a metal cylinder (see *a*, fig. 1). The filament may be of any voltage, but I find it most convenient to employ filaments of such a length and section that they are brought to bright incandescence by an E.M.F. of 12 volts. The voltage and section of the filament should be so arranged that the temperature of the filament corresponds with an "efficiency," as a lamp-maker would say, of 2·75 or 3 watts per candle. The filament is conveniently brought to incandescence by a small insulated battery of secondary cells. A circuit is then completed through the vacuous space in the bulb between the cylinder and the filament by another wire which joins the external terminal *t* of the metal cylinder and that terminal of the carbon filament which is in connection with the negative pole of the heating battery. In this last circuit is placed a sensitive mirror galvanometer of the movable needle or movable coil type, and also a coil which may

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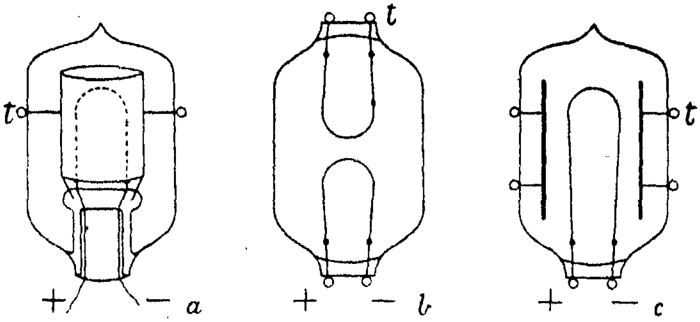
vol. 13, Part LXXXIV, p. 45, Friday evening discourse on February 14, 1890, "Problems on the Physics of an Electric Lamp," when this unilateral conductivity was experimentally shown.

be the secondary circuit of an air core transformer in which electric oscillations are set up. As is now well known, the vacuous space in the bulb permits negative electricity to move in it from the hot filament or cathode through the vacuous space to the cylinder or anode and back through the galvanometer and coil, but not in the reverse direction, as long as the cylinder is cool and the carbon filament not at a temperature much above the melting point of platinum. To illustrate the action of the bulb as an electrical valve, the following experiments can be shown:—

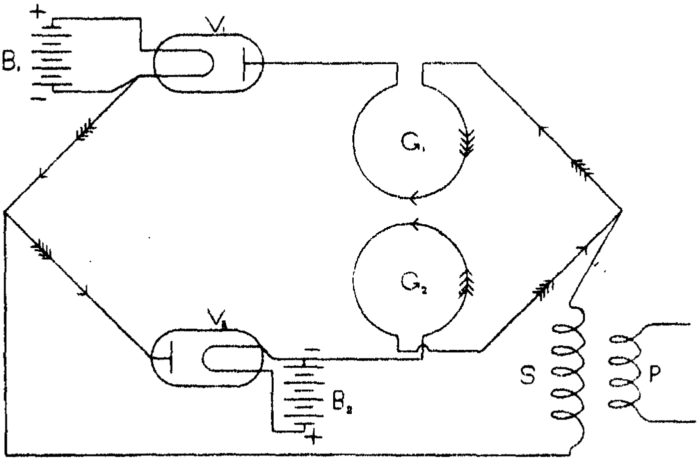
Electric oscillations are set up in a metal wire circuit by the discharge of a Leyden jar, as usual. This circuit takes the form of a thick wire of one or more turns, bent into the form of a circle or square. Some distance from this, we place another wire, of several, say eight or ten turns, also bent into the form of a circle, and connect this last wire into the circuit of a galvanometer and vacuum bulb made as described, so that it is a circuit having unilateral conductivity. On exciting the oscillations in the primary circuit by an induction coil we have an alternating high frequency magnetic field produced, which affects the secondary circuit at a distance. The oscillations in this last are, however, able to flow only in one direction. Hence, the galvanometer is acted upon by a series of intermittent but unidirectional electromotive forces, and its needle or coil deflects. Since the field is a high frequency field, we can show the screening effect of a sheet of tin foil or silver paper in a very simple and effective manner by the effect it produces in cutting down the galvanometer deflection when the metal sheet is interposed between the primary secondary circuits. Also, if we move the secondary coil away from the primary coil or turn the two coils with their planes at right angles to one another, then the galvanometer deflection diminishes or falls to zero because the induction is decreased. Accordingly, we have in this vacuum valve and

Fig. 1.



associated mirror galvanometer a means of detecting feeble alternating electric currents or oscillations. Another method is to employ a differential galvanometer and two vacuum valves. These must then be arranged, as shown in fig. 2, one circuit G_1 of the differential galvanometer is in series with one valve V_1 and the other circuit G_2 with the other valve V_2, but so joined up that currents flowing through the valves in opposite directions pass round the two galvanometer wires in the same direction as regards the needle and, therefore, their effects are added together on the galvanometer needle. Each valve must then have its own separate insulated battery to ignite the filament. Also, it is necessary that the connection with the oscillatory circuit must be made in both cases to the hot filament by that terminal which is in connection with the negative pole of the local battery used to ignite the filament (see fig. 2).

Fig. 2.



This arrangement of a differential galvanometer and two valves transforms, of course, more of the alternating oscillation into direct current than when one valve alone is used. It provides us with a means of detecting electrical oscillations not merely in closed circuits but in open electrical circuits.

When so using it, it is necessary to associate with the oscillation valve and galvanometer an oscillation transformer for raising the voltage. The resistance of these valves, when in operation, may be anything from a few hundred ohms up to some megohms, depending on the state of incandescence of the filament and upon the electromotive force employed to drive the current through the vacuous space, as well as upon the size of the filament and the plate. This resistance does not obey Ohm's law, but the current increases to a maximum and then slightly decreases as the voltage progressively increases. The form of oscillation transformer employed with the device is as follows: A small air-core induction coil has a primary circuit, which consists of 52 turns of gutta-percha covered wire, wound in a helical groove cut on an ebonite rod 0·5 inch in diameter and 6 inches in length. The primary circuit is made of a No. 20 or No. 22 S.W.G. copper wire. The secondary circuit consists of 36,000 turns of fine silk-covered wire, No. 36, wound in six coils, each having about 6000 turns, and all joined in series. This secondary circuit has one terminal connected to one common terminal of the galvanometer and the other to the common terminal of the two oscillation valves (see fig. 4). The primary coil of this oscillation transformer has one terminal connected to earth and the other to a long insulated rod which acts as an aerial or electric wave collector. To prevent the direct action of the transmitter upon the secondary coil by simple electromagnetic induction, it is best to wind the secondary coil in two equal parts in opposite directions and to wind the primary in a corresponding manner.

If an electric wave sent out from a similarly earthed transmitter falls upon the rod, then an electrical oscillation is set up in the receiving circuit and therefore in the primary coil of the oscillation transformer inserted in series with it. This oscillation is raised in voltage by the secondary coil of the transformer, and by reason of the unilateral conductivity of a vacuum valve, placed in series with the coil, one part of the oscillation, viz., the positive or the negative current, passes round the galvanometer coils and affects it.

If we employ a sensitive dead beat galvanometer of the type called by cable engineers a "Speaking Galvanometer," then intelligible signals can be sent by making small and larger deflections of the galvanometer corresponding to the dot and dash of the Morse alphabet; anyone who can "read mirror" can read off the signals as quickly as they can be sent on an ordinary short submarine cable with this arrangement.

The arrangement, although not as sensitive as a coherer or magnetic detector, is much more simple to use. Also it has one great advantage, viz., that it enables us to examine the behaviour of any particular form of oscillation producer. By means of it we can detect changes in the wave-making power or uniformity of operation of the transmitting arrangement, by the variation of the deflection of the galvanometer. Thus, for instance, if a spark-ball transmitter is being employed and the deflection of the galvanometer in association with the receiving aerial is steady, if we put the slightest touch of oil upon the spark-balls of the transmitter, their wave-making power is increased and the deflection of the galvanometer at once increases. Since the current through the galvanometer is the result of the groups of oscillations which are created in the receiving circuit, and since in the ordinary *transmitter these oscillation groups are separated by wide intervals of* silence, it is obvious that we can increase the sensitiveness of the above described arrangement by employing a very rapid break or interruptor with the induction coil. If, for instance, we employ a Wehnelt break with the induction coil or a high speed mercury break or alternating current transformer, we get a far better result as indicated by the deflection of the galvanometer than when employing the ordinary low frequency spring or hammer break.

The point of scientific interest in connection with the device, however, is the question how far such unilateral conductivity as is possessed by the vacuous space is complete. The electrical properties of these vacuum valves have accordingly been studied.

A bulb containing a 12-volt carbon filament rendered brightly incandescent by a current of about 2·7 to 3·7 ampères was employed. The filament was surrounded by an aluminium cylinder. The length of the carbon filament was 4·5 cm., its diameter 0·5 mm., and surface 70 square mm.

The aluminium cylinder had a diameter of 2 cms., a height of 2 cms., and a surface of 12·5 square cms. The filament was shaped like a horse-shoe, the distance between the legs being 5 mm. This filament was rendered incandescent to various degrees by applying to its terminals 8, 9, 10, and 11 volts respectively. Another insulated battery of secondary cells was employed to send a current through the vacuous space from the cylinder to the filament, connection being made with the negative terminal of the latter. The current through the vacuous space and the potential difference of the cylinder and negative end of the hot carbon filament were measured by a potentiometer. The effective resistance of the vacuous space is then taken to be the ratio of the so observed potential difference (valve P.D.) to the current (valve current) through the vacuum.

The following table records the observations. The column headed P.D. gives the potential difference between the hot filament and the cylinder, that headed A gives the current through the vacuous space in milliampères, that headed R the resistance of the space in ohms, and that headed $K10^5$ is 100,000 times the conductivity.

The result is to show that the vacuous space does not possess a constant resistance, but its conductivity increases rapidly up to a maximum and then decreases as the valve potential difference progressively increases. If we plot the current values as ordinates and potential difference of the valve electrodes as abscissæ, we find that the current curve quickly rises to a maximum value and then falls again slightly as the potential difference increases steadily. The conductivity curve also rises to a maximum and then decreases (see fig. 3).

The facts so exhibited are well-known characteristics of gaseous

Table I.—Variation of Current through, and Conductivity of, a Vacuum Valve with varying Electromotive Force, the Electrodes being an Incandescent Carbon Cathode and Cool Aluminium Anode.

Carbon filament at 11 volts, 3·77 amp., 41·47 watts.				Carbon filament at 10 volts, 3·44 amps., 34·43 watts.			
Vacuum Space.				*Vacuum Space.*			
P.D.	A.	R.	$K10^5$.	P.D.	A.	R.	$K10^5$.
0·6	0·024	25,000	4·0	0·7	0·014	50,000	2·0
5·4	0·264	20,550	4·86	2·8	0·073	38,360	2·6
8·8	0·480	18,330	5·45	8·2	0·392	20,920	4·76
18·2	3·880	4,691	21·4	12·8	0·824	15,530	6·56
22·9	26·790	855	118·1	16·2	1·739	9,316	10·70
29·1	28·02	1,038	96·1	20·1	5·352	3,756	26·6
37·1	28·426	1,305	76·6	23·3	9·68	2,407	41·4
49·0	26·50	1,719	58·0	35·9	10·037	3,577	28·0
70·2	26·87	2,613	38·3	49·7	9·794	5,075	20·0
100·0	24·36	4,105	25·0	71·6	8·920	8,027	12·5
				100·08	8·331	12,010	8·32

Carbon filament at 9 volts, 3·112 amps., 28·0 watts.							
Vacuum Space.							
P.D.	A.	R.	$K10^5$.	P.D.	A.	R.	$K10^5$.
0·5	0·005	100,000	1·0	24·2	2·389	10,130	10·0
2·5	0·049	50,020	2·0	28·2	2·437	11,650	8·6
5·2	0·128	40,625	2·46	36·6	2·508	14,590	6·86
8·3	0·324	25,620	4·0	48·6	2·535	19,170	5·0
8·8	0·361	24,380	4·1	58·5	2·374	24,640	4·0
12·6	0·70	17,970	5·5	72·5	2·258	32,180	3·0
16·4	1·735	9,452	10·6	102·0	2·067	49,350	2·0
20·4	2·351	8,677	11·2				

conduction in rarified gases.* It may be noted that there is in these current-voltage and voltage-conduction curves a general resemblance to the magnetisation and permeability curves of iron.

To examine further the nature of this conduction, the following experiments were made. If a vacuum bulb, as described, is joined up in series with a galvanometer and an electrodynamometer and an alternating electromotive force applied to the circuit, the two instruments will both be affected. The galvanometer is, however, affected only by

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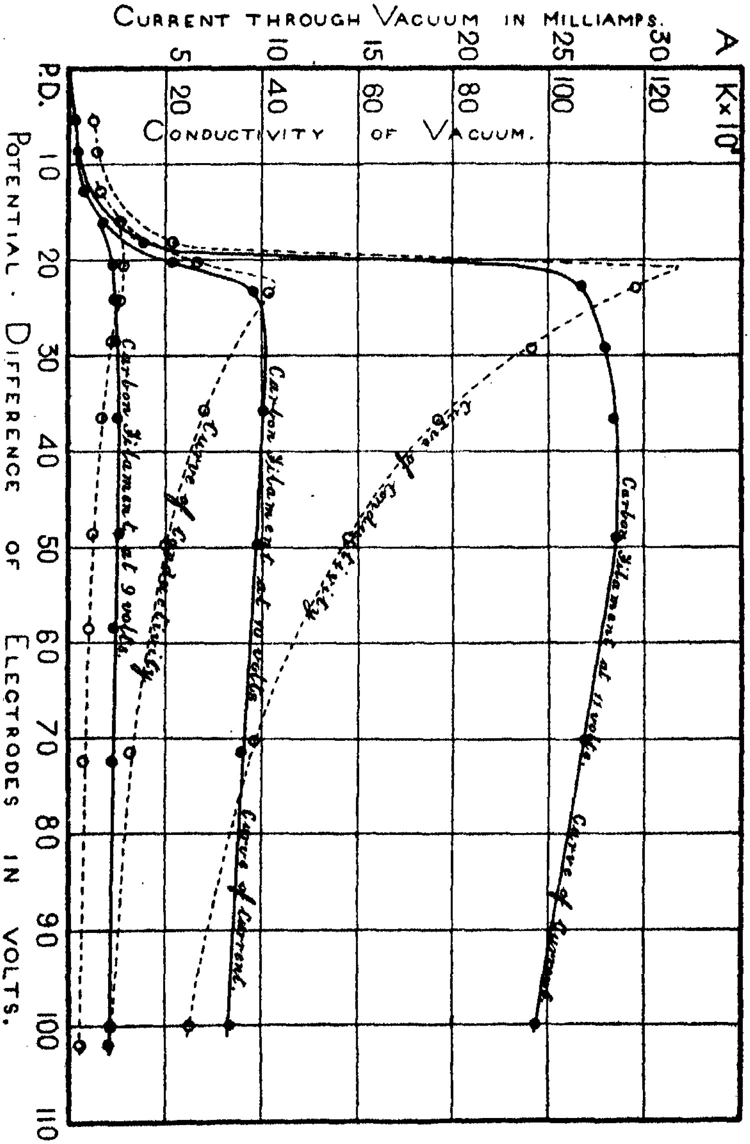
* See J. J. Thomson, 'Conduction of Electricity through Gases,' Chap. VIII.

FIG. 8.



the resultant flux of electricity in one direction. It measures the unidirectional current. The dynamometer is affected by the bilateral flux of electricity and it measures the total or alternating current. If, therefore, the vacuous space is totally non-conducting in one direction, one half of the alternating current will be cut out. The galvanometer will read the true mean (T.M.) value of the remanent unidirectional current, and the dynamometer will read the root-mean-square (R.M.S.) value. If the conductivity in one direction is not zero, then the galvanometer will read the T.M. value of the difference of the positive and negative currents, but the dynamometer will read the R.M.S. value of their sum.[*]

In the last case, the current through the valve may be considered to be a continuous current superimposed upon an alternating current.

If we call I the maximum value of the nearly sinoidal current in one direction, and I′ the maximum in the opposite direction, then we may say that the dynamometer reading (D) expressed in true current value is equal to $g\,(\mathrm{I}+\mathrm{I}')$ where g is the *amplitude factor*, and also that the galvanometer reading (G) in true current value is equal to $g/f\,(\mathrm{I}-\mathrm{I}')$ where f is the *form factor* of the current.[†] Hence—

$$\frac{\mathrm{D}}{\mathrm{G}} = f\frac{\mathrm{I}+\mathrm{I}'}{\mathrm{I}-\mathrm{I}'}, \quad \text{or} \quad \frac{\mathrm{D}/\mathrm{G}+f}{2f} = \frac{\mathrm{I}}{\mathrm{I}-\mathrm{I}'}.$$

The fraction $\dfrac{2f}{\mathrm{D}/\mathrm{G}+f}$, say β, expressed as a percentage may be called the *rectifying power* of the valve, for it expresses the percentage which the actual unilateral electric flow or continuous current through the valve is of that continuous current which would flow if the unilateral conductivity were perfect.

Perfect rectifying power, however, does not exist. There is not an infinite resistance to movement of negative electricity from the metal cylinder to the hot filament through the vacuum, although this resistance is immensely greater than that which opposes the movement of negative electricity in the opposite direction. This point was examined, as follows: A very sensitive electrodynamometer was skilfully constructed by my assistant, Mr. G. B. Dyke, the fixed coil having 2000 turns of No. 47 silk-covered copper wire and the movable coil 1000 turns. The suspension of the movable coil was by a fine flat phosphor-bronze wire at top and bottom. The deflection was observed by a mirror and scale.

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[*] If i is the instantaneous value of a periodically varying current with maximum value I and periodic time T, then the root-mean-square value (R.M.S. value) of i is defined to be $\left(\frac{1}{\mathrm{T}}\int_0^{\mathrm{T}} i^2dt\right)^{\frac{1}{2}}$ and the true mean value (T.M. value) of i is defined to be $\frac{2}{\mathrm{T}}\int_0^{\frac{1}{2}\mathrm{T}} idt$.

[†] The *form factor f* and *amplitude factor g* are the names given by the author (see 'Alternating Current Transformer,' J. A. Fleming, vol. 1, p. 585, 3rd edit.) to the ratio of the R.M.S. to the T.M. value of the ordinates of a single valued periodic curve, and to the ratio of the R.M.S. value of the ordinates to the maximum value during the period.

This dynamometer was placed in series with a shunted movable coil galvanometer of Holden-Pitkin pattern, and the two together placed in series with a variable section of an inductionless coil through which an alternating current was passing. A vacuum valve as above described was in series also with the galvanometer and dynamometer. The alternating current was derived from an alternator giving a nearly true sinoidal electromotive force. The form factor of the electromotive force curve of this alternator was determined and found to be 1·115, that for a true sine curve being 1·111.

The vacuum valve sifted out the alternating current flow and allowed the currents in one direction to pass, but nearly stopped those in the opposite direction. The indications of the electrodynamometer were proportional to the root-mean-square (R.M.S.) value of the sum of the two opposite currents, and that of the galvanometer to the true mean value (T.M.) of their difference. The galvanometer and dynamometer were both calibrated by a potentiometer by means of continuous current, and curves constructed to convert their scale readings to milliampères. Then with various alternating current electromotive forces, their readings were taken when in series with a vacuum valve and recorded in the following tables. The letter D denotes current in milliampères as read by the so calibrated dynamometer and G that read by the galvanometer. The ratio D/G is denoted by α, and the rectifying power, viz., $2f/\alpha+f$ by β.

The table shows that the value of α is not constant, but for each state of incandescence of the filament reaches a maximum which, however, does not greatly differ from the mean value for the range of currents used. If we set out the mean values of β in a curve (see fig. 4), in terms of the power expended in heating the carbon filament, we see that the rectification is less complete in proportion as the temperature of the carbon filament increases. This is probably due to the fact that as the filament gets hotter, it heats the enclosing cylinder to a higher temperature and enables negative electricity to escape from the latter.

Hence, I feel convinced that if the metal cylinder could be kept quite cool by water circulation the rectification would reach 100 per cent. or be complete.

An ideal and perfect rectifier for electric oscillations may, therefore, be found by enclosing a hot carbon filament and a perfectly cold metal anode in a very perfect vacuum. With a bulb such as that used for the above experiments all we can say is that the current passed through the vacuum is from 80 to 90 per cent. continuous, 100 per cent. implying that the vacuum is perfectly non-conducting in one direction and permits the flow of negative electricity only from the hot to the cold electrode. The necessity for keeping the cathode cold is shown by the following experiment :—An alternating-current arc was

Table II.—Ratio of Electrodynamometer (D) to Galvanometer (G) Readings in Milliampères. Form Factor of E.M.F. Curve = 1·115 = f.

Carbon filament at 11 volts, 3·77 amps., 41·7 watts.

D.	G.	$D/G = \alpha$.	$2f/\alpha + f = \beta$.	
0·85	0·57	1·49	0·86	Mean = 0·82.
1·33	0·85	1·56	0·83	
1·87	1·16	1·61	0·82	
2·30	1·40	1·64	0·81	
3·20	1·88	1·73	0·78	
3·52	2·10	1·68	0·80	
4·54	2·81	1·62	0·82	

Carbon filament at 10 volts, 3·44 amps., 34·43 watts.

D.	G.	$D/G = \alpha$.	$2f/\alpha + f = \beta$.	
0·50	0·34	1·47	0·86	Mean = 0·83.
1·34	0·86	1·56	0·83	
2·28	1·48	1·54	0·84	
2·72	1·68	1·62	0·82	
2·78	1·71	1·63	0·81	
3·02	1·87	1·62	0·82	
3·53	2·17	1·63	0·81	
4·30	2·92	1·47	0·86	
4·25	2·88	1·48	0·86	

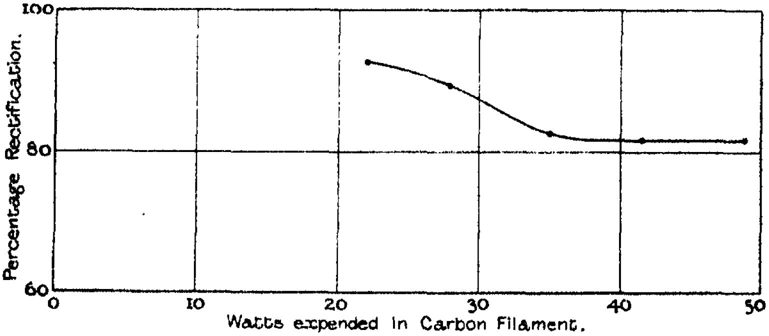
Carbon filament at 9 volts, 3·112 amps., 28·0 watts.

D.	G.	$D/G = \alpha$.	$2f/\alpha + f = \beta$.	
0·40	0·31	1·29	0·93	Mean = 0·89.
0·73	0·50	1·46	0·87	
1·28	0·83	1·54	0·84	
1·65	1·15	1·43	0·88	
1·82	1·26	1·44	0·87	
1·78	1·26	1·41	0·88	
1·93	1·35	1·43	0·88	
1·94	1·41	1·38	0·89	
1·87	1·41	1·38	0·91	
1·83	1·39	1·32	0·92	
1·73	1·37	1·26	0·94	

formed between carbon rods, and an iron rod was placed so that its end dipped into the arc. An ammeter was connected in between either carbon and the iron rod, and indicated a continuous current of negative electricity flowing through the ammeter from the iron rod to the carbon pole. This current was, however, greatly increased by making the iron rod of a piece of iron pipe closed at the end and kept cool by a jet of water playing in the interior. In this manner I have been able to draw off a continuous current of 3 or 4 ampères from an alternating-current arc using 15 alternating-current ampères.

Returning, then, to the vacuum valve, we may note that the curves in fig. 3 show that the vacuous space possesses a maximum conductivity corresponding to a potential difference of about 20 volts between the electrodes, for the particular valve used. The interpretation of this fact may, perhaps, be as follows:—In the incandescent carbon there is a continual production of electrons or negative ions by atomic dissociation. Corresponding to every temperature there is a certain electronic tension or percentage of free electrons. If the carbon is made the negative electrode in a high vacuum these negative ions are expelled from it, but they cannot be expelled at a greater rate than they are produced. Therefore, there is a maximum value for the outgoing current and a maximum value for the ratio of current to electromotive force, that is for the conductivity.

FIG. 4.



This fact, therefore, fixes a limit to the utility of the device. The current through the vacuous space is, to a very large extent, independent of the electromotive force creating it, and is at no stage proportional to it, or at least only within a narrow range of electromotive force near to the maximum conductivity.

Whilst, therefore, the device is useful as a simple means of detecting electric oscillations, it has not that uniformity of conductivity which would make it useful as a strictly metrical device for measuring them. It can, however, perform the useful service of showing us how far any device for producing electric oscillations or electric waves produces a uniform or very irregular train of electric oscillations, and what changes conduce to an improvement or reduction in the efficiency of the transmitting device.

"On an Instrument for the Measurement of the Length of Long Electric Waves, and also Small Inductances and Capacities."

By J. A. FLEMING, M.A., D.Sc., F.R.S., Professor of Electrical Engineering in University College, London. Received January 26,—Read February 9, 1905.

The measurement of the length of the waves used in connection with Hertzian wave telegraphy is an important practical matter. Since the wave-length of the radiated wave is determined by the frequency of the electric oscillations in the radiator, the determination of this frequency is all that is required. The principle of resonance is generally called into assistance to effect this measurement. It may be done by the employment of either an open or a closed resonant circuit.

Instruments for this purpose have been devised in which some circuit having capacity (C) as well as inductance (L) in series with each other, has one or both these factors altered until the electrical time-period of the circuit agrees with that of the wave making circuit. Since this agreement depends upon the equality of the product $\sqrt{CL}$ for the two circuits, the author proposes to call this quantity $\sqrt{CL}$ the *oscillation constant* of the circuit and the number of oscillations in 2π seconds or $2\pi n$, where n is the frequency, the *oscillation number*. Then it is a property of simple oscillatory circuits that the product of the oscillation number and oscillation constant is unity. Some means has, therefore, to be employed to indicate when the adjustment of the two factors of the adjustable circuit has brought its oscillation constant into agreement with that of the transmitter circuit. In a wave-meter devised by J. Dönitz,[*] which is of the closed circuit form, a condenser of variable capacity has its terminals short-circuited by an inductance coil, and this coil is acted upon inductively by some part of the transmitter circuit so that oscillations are set up in it. A variation of the capacity is made until the root-mean-square value of the current in its circuit is a maximum. This is done by the employment of a sensitive form of hot wire ammeter.

There are, however, some objections to this form of wave-meter, and especially to the use of a hot wire ammeter. The root-mean-square value of the oscillation depends not only upon the maximum value and logarithmic decrement of the oscillations, but upon the number of groups of oscillations per second. Hence, if the discharger of the transmitter is an ordinary spark discharger, the variation of the oscillations due to variation in the break speed or spark-ball surfaces and, therefore of the root-mean-square value of the current set up in the wave-meter circuit will be considerable. There is, therefore, some difficulty in finding the position of adjustment sharply.

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[*] See J. Dönitz, "On Wave Meters and their Uses," 'Elecktrotechnische Zeitschrift,' vol. 24, p. 920, 1903, Nov. 5; also 'The Electrician,' vol. 52, p. 407, Jan. 1, 1904.

Another point calls for attention. It is well known, from the theory of syntonised circuits, that if two circuits having capacity and inductance are brought into inductive relation to each other, the resulting complex circuit has two time-periods of oscillation. Even if the two circuits when separate and far removed have their time-periods adjusted to equality, the resulting time-period when they are brought into inductive relation to each other differs from the common value. There are, in fact, two frequencies in the coupled circuit, one greater and the other less than the common period. These, however, tend to equality and to indentity with the free independent period of each circuit separately in proportion as the mutual induction between the coupled circuits is reduced.* The object, therefore, held in view in designing the instrument here described was to construct one which, whilst having a fairly large inductance of its own, should be capable of being associated with the circuit to be tested, and set in action by it, by means of a mutual inductance as small as possible.

This has been achieved by making the part of the circuit of the instrument which is acted upon inductively by the circuit to be tested only a small part of the circuit on which its whole inductance depends. We are thus able to keep the self-inductance large and the mutual inductance small, and therefore prevent any great reaction of the secondary current upon the circuit which is being tested.

A closed circuit wave-meter has been devised on these lines by the author, employing a neon vacuum tube detector, which enables the measurement of the oscillation-constant of the transmitter circuit to be made with great accuracy and quickness, and is also useful for measuring small inductances and capacities.†

It is constructed in one form, as follows:—An ebonite tube, about 100 cms. long, has cut upon its outer surface a screw groove having 1·6 turns per centimetre and a length of 60 cms. is cut. In this groove is wound a bare copper wire, SS. No. 14 S.W.G. size (see fig. 1), one end of the wire is attached to a metal pin p_1 which forms a bearing supporting the tube, and the other end of the wire is insulated. To this latter end of the ebonite tube is attached a brass tube I 60 cms.

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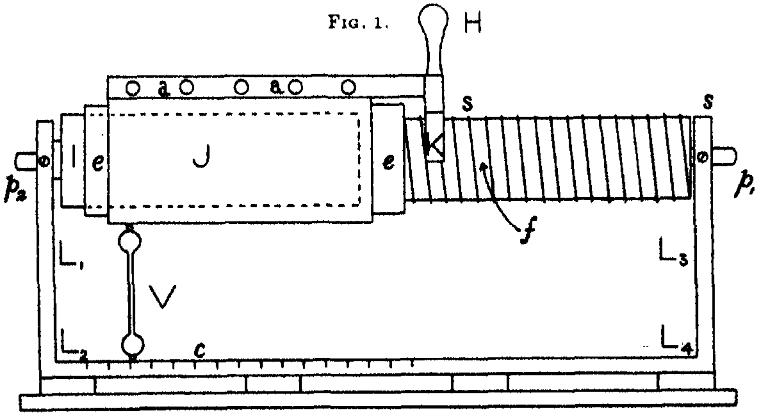
* See A. Oberbeck, "Ueber den Verlauf der Electrischen Schwingungen bei den Tesla'schen Versuchen," 'Wied. Annalen der Physik,' vol. 55, p. 627, 1895.

† The use of a neon vacuum tube as a sensitive indicator of a high-frequency electric field was mentioned first in a paper read by the author to the British Association at Cambridge, September, 1904. The author is indebted to Sir William Ramsay for two tubes of this gas. Sir James Dewar has shown that such neon vacuum tubes can be readily prepared from atmospheric air by the employment of absorbent charcoal at very low temperatures. It would be an advantage if the manufacture of these neon tubes could be placed on a commercial basis, in view of their utility for the purposes here described.

in length and 8 cms. outside diameter. Over this brass tube is placed an ebonite tube *ee* the sides of which are 5 mm. in thickness and its length 80 cms. This ebonite tube fits tightly on the brass tube. The brass tube is closed at the end remote from the inductance coil by a plate and a pin p_2 which forms a bearing for the whole apparatus. Over the larger ebonite tube is slipped a metal cylinder or outer jacket J which can slide easily on the ebonite tube. This jacket carries a rod ending in a half-collar of metal K resting on the inductance spiral (see fig. 2). An ebonite handle H enables the jacket to be moved to and fro. It will be seen, therefore, that the arrangement constitutes a condenser formed of the inner and outer brass tubes separated by an ebonite dielectric, the capacity of which can be varied by moving the outer jacket away from the inner. Also this condenser is in series with an inductance coil, the inductance of which is reduced or increased by the same movement which reduces or increases the capacity. The oscillation constant of the arrangement is, therefore, variable between certain limits, and its variation with the displacement of the handle H follows a straight line law.

Fig. 1.



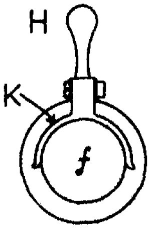


Fig. 2.

The pins p_1, p_2 (see fig. 1) which form, respectively, one of the terminations of the inductance and capacity, are connected together by a stout copper bar L_1, L_2, L_3, L_4, so completing the electric circuit, the capacity and inductance of which can be varied. In order to detect the condition in which the oscillations have a maximum value in this circuit, a vacuum tube V is employed (see fig. 1), which may preferably be a vacuum tube containing neon, or failing that, a tube containing rarified carbonic dioxide may be used, the glass being uranium. This vacuum tube should be constructed with two bulbs and with a narrow tubular portion like a spectroscope tube. It may be attached to the outer brass jacket as in fig. 1, or it may be attached to a bar connected with the inner brass tube, the vacuum tube being hung over the outer jacket. Also a scale is provided showing the position of the sliding jacket and which, therefore, can be graduated to show the oscillation constant of the arrangement for various positions of the jacket.

Supposing then that we desire to determine the frequency of the oscillations in any wire such as a Marconi aerial wire used in Hertzian-wave telegraphy, part of this wire is laid alongside the copper bar and the oscillations in it induce others in the circuit of the wave-meter. The oscillation constant is then varied by moving the outer jacket by means of the insulated handle H until the vacuum tube V glows most brightly. If proper adjustments are made of the position of the vacuum tube, it will be found that the tube does not shine at all until the outer jacket J is within a few millimetres of the position in which the oscillation constant of the instrument agrees with that of the circuit being tested. By taking two or three readings with the jacket, a little too far one way and a little too far the other way and approaching the right position from both sides and taking the mean scale reading, it is possible to obtain the oscillation constant with great accuracy. If the capacity is measured in microfarads and the inductance in centimetres, then it will be found that the oscillation constant required is generally some number lying between 1 and 20. The instrument already constructed by the author on this pattern is adapted for the determination of oscillation constants lying between 0·16 and 7·5.

In the case of Hertzian-wave telegraphy conducted on Marconi principles, the wave-length employed, reckoned in feet, is equal to 195·8 times the oscillation constant of the transmitter circuit, or reckoned in metres, to 59·73 times the oscillation constant. Hence, the above described instrument is capable of measuring wave-lengths from 30 to 1500 feet, and might easily be constructed to measure wave-lengths of any greater length.*

By a slight modification, the instrument can be constructed more simply as follows: A single ebonite tube is employed which may be a metre or a metre and a-half in length and 10 cms. outside diameter, the thickness of the walls being about 5 mm. On this tube is wound as before an inductance coil of 100 or 200 turns of No. 14 S.W.G. bare copper wire. Also the tube is provided with an outer jacket or brass outer tube J (see fig. 3). This is conveniently formed out of the sheet of thin brass bolted round the tube, and one end of the inductance coil SS is attached to this jacket, the other end of the coil being attached to a brass ring *d*, carrying an ebonite handle H. In the interior of this ebonite tube, at one end, there is an inner brass tube I which can slide easily in and out of the ebonite tube *e*. This brass tube has a pin *p* fixed at one end, by which it is attached to a copper bar L_1, L_2, L_3, L_4, ending in a curved crutch or collar K on which the inductance spiral rests (see fig. 4). The other arrangements are as in the instrument already described.

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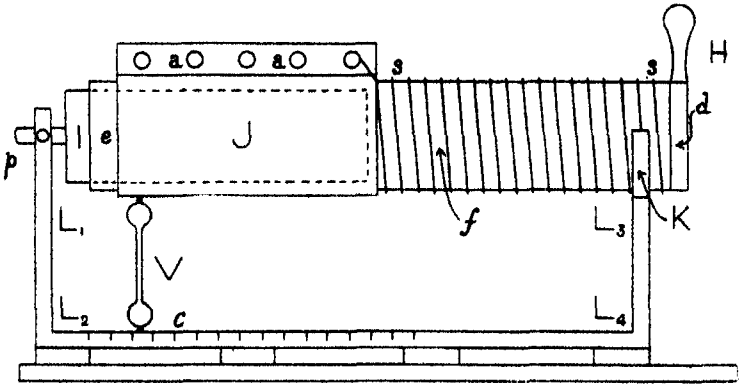
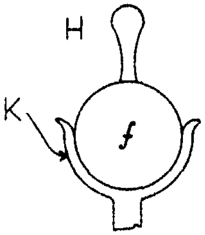
* *February* 11, 1905.—The author has since constructed one to measure electric waves up to 2400 feet in length.

FIG. 3.



The only differences between the forms shown in fig. 1 and fig. 4 are that in fig. 1 the outer metal jacket is movable and the inner one is fixed, whereas in the second form, the outer jacket is fixed with respect to the inductance coil, and the two together are drawn away from the inner brass tube, thus reducing the capacity and inductance at the same time. The instrument is very convenient for the measurement of small inductances. Thus, for instance, suppose it is desired to measure the inductance of a wire for high frequency currents, the wire having an inductance of not more than a few hundred centimetres, that is to say, something of the order of a microhenry, this inductance may be measured by the instrument in the following manner:—An insulated wire AB (see fig. 5) is laid alongside the copper bar L_2, L_4, and the circuit of the wire is completed by a condenser C of known capacity and a spark gap S. Oscillations are then set up in this condenser and wire by means of an induction coil as usual, and the handle H is shifted until the vacuum tube V glows or glows most brilliantly. We then know that the oscillation constant of the instrument in that position agrees with that of the circuit so formed. When that is the case, the oscillation constant of the wave-meter can be read off in the scale attached to it, and we, therefore, know the oscillation constant (call it O) of the circuit formed by the condenser and the wire. Hence, if C is the capacity of the condenser in that circuit and L is the inductance of the wire of the circuit, then $O = \sqrt{CL}$. If, then, we increase the inductance L by adding in series with it a wire of which the inductance is desired (call it L′), we can

FIG. 4.



then shift the handle H until we get a fresh agreement and find a second value O′ for the oscillation constant of the circuit. Then we have

$$O' = \sqrt{C(L+L')}.$$

Hence

$$L' = \frac{O'^2 - O^2}{C}.$$

As an illustration the following test measurement was made. A copper wire, the diameter (d) of which was 0·128 or 0·32 cm. was bent into a nearly complete circle 70 cms. in diameter. The inductance of this wire can be calculated from the formula

$$L' = 2\pi D\left(\log_e \frac{4\pi D}{d} - 2{\cdot}45\right) + \frac{R'}{2\pi n}.$$

In the above case $D = 70$ cms., and $d = 0{\cdot}32$ cm., and R′ is the resistance of the wire to oscillations having a frequency n. The value of L′ is then 2400 cms. This wire was joined in series with another wire laid alongside the bar L_2, L_4 of the measuring instrument and a condenser having a capacity of 0·00146 microfarad joined up in series with the circuit and a spark gap. The instrument was then used to determine the oscillation constant O′ of the circuit with the circular wire included, and the oscillation constant O when the circular wire was not included. It was found that O′ = 3·5 and O = 3·0. Whence

$$L' = \frac{12{\cdot}25 - 9}{0{\cdot}00146} = 2226 \text{ cms.,}$$

a value in fairly close agreement with the calculated value, considering that the inductance is less than 2·5 microhenrys.

In this manner it is possible to determine the inductance of a foot or two of coiled copper wire for high frequency currents with fair accuracy. The oscillation constant of an instrument of the above form for various positions of the outer jacket or inner jacket, according to the form used, can best be determined directly by means of a standard wave-meter, such as that described by the Author in a paper to the British Association at Cambridge, September, 1904.*

In this last mentioned arrangement, a long ebonite tube is wound over uniformly with a fine silk-covered copper wire in closely adjacent turns and in one layer. The capacity and inductance per unit of length (c and l) of this long helix must then be determined by known methods, and from this measurement we can determine the velocity of propagation of an electric wave along the helix, for it is equal to the reciprocal of the square root of the product of the capacity and inductance per unit of length of the helix. If we form an oscillatory circuit (see fig. 5), consisting of a condenser, C, a variable inductance, L, and a spark gap, S, the variable inductance including a length of straight wire AB, which can be placed parallel with, and close to, the copper bar of the form of wave-meter described in this paper, then we can bring its oscillation constant into agreement with the oscillation constant of the circuit formed of the variable inductance and condenser. In order to determine the value of this oscillation constant we connect the long helix above described to one terminal of the condenser of the oscillating circuit above described, one spark ball being to earth. The arrangement must be as shown in fig. 5. The long helix of insulated wire HH is then provided with a sliding metal saddle D, which can be connected to the earth E, and this saddle is moved along the helix until a position is found such that by means of a neon or other sensitive vacuum tube V, we can detect a node of potential half-way between the saddle and the point of attachment of the helix to the oscillating circuit, the saddle itself being connected to the earth will also be a node of potential. Hence the distance between the saddle and the end of the helix attached to the oscillating circuit is equal to one wave-length of the wave travelling along the helix.

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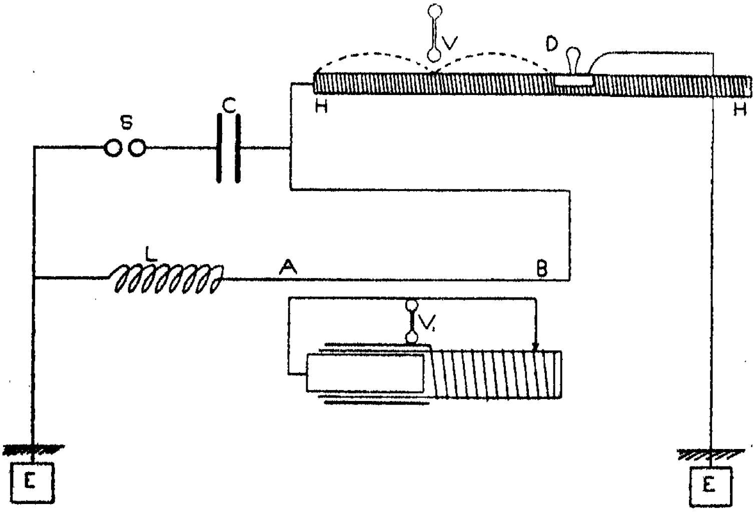
* See J. A. Fleming, "On the Propagation of Electric Waves along Spiral Wires, and on an Appliance for Measuring the Length of Waves used in Wireless Telegraphy," 'Phil. Mag.,' October, 1904.

If W is the velocity of the wave along the helix and λ is the wave-length of the stationary wave, as measured on the helix, and n the frequency of the oscillations, then $W = n\lambda$. If C is the capacity and L the inductance in the oscillatory circuit formed with the condenser of unknown capacity and variable inductance, then the frequency in this circuit is $n = 1/2\pi\sqrt{CL}$.

Also if c and l are the capacity and inductance per unit of length of the long helix, we have $W = 1/\sqrt{cl}$. Therefore

$$\frac{1}{\sqrt{cl}} = \frac{\lambda}{2\pi\sqrt{CL}}, \quad \text{or} \quad \sqrt{CL} = \frac{\lambda}{2\pi}\sqrt{cl}.$$

FIG. 5.



Hence, since λ can be measured, and the oscillation constant of the helix per unit of length $\sqrt{cl}$ is known, we have the oscillation constant of the exciting circuit, and therefore of the closed circuit wave-meter in any position when it is adjusted to agree with that circuit. Otherwise, if we have the means at hand, the oscillation constant of the instrument can be determined for various positions of the slider by simply measuring the capacity (C) of the condenser and inductance (L) of the helix which are effective in that position, and calculating the value of $\sqrt{CL}$ for various positions of the outer or inner jacket, according to the form of instrument used. The instrument can have its scale marked to show directly either oscillation constants (O) or frequencies (n), or aërial wave lengths (λ) in metres or feet. The instrument is not only useful for quantitative work in connection with Hertzian-wave telegraphy, but is very useful in the laboratory for the determination of the coefficients of coupling and mutual inductances of oscillation transformers.

If there be two circuits inductively connected, forming an air core transformer or oscillation transformer, and if these circuits have respectively coefficients of self-induction L and N, and a coefficient of mutual induction M, then we can determine L and N and M, if these are not too large, by the instrument, and also the "coefficient of coupling" of the transformer, viz., $M/\sqrt{LN}$.

For this purpose we connect the two circuits of the transformer in two ways. 1st, so that a current sent through the circuit flows round in the same direction in the two coils; and 2nd, so that it flows in the opposite direction in the two coils. In the first position, the effective inductance of the whole system is L_1, where $L_1 = L + 2M + N$, and in the second position it is L_2, where $L_2 = L - 2M + N$. Hence, $L_1 + L2 = 2(L + N)$, and $L_1 - L_2, = 4M$. Accordingly, we make four inductance measurements with the instrument. 1st, that of the primary coil alone, the secondary being open; 2nd, that of the secondary alone, the primary being open; 3rd, that of the primary and secondary together joined up to assist; and 4th, that of the primary and secondary together, joined up to oppose.

Twice the sum of the first two measurements should agree with the second, and one quarter of the difference of the last two gives the mutual inductance. Having therefore L, M, and N, we can calculate the coupling, $M/\sqrt{LN}$.

In making measurement of this kind with high frequency currents it is necessary to bear in mind that we cannot obtain the true separate inductance of the primary coil simply by measuring it with the secondary coil over it, even if that secondary coil has its terminals open. There is a quite sensible dielectric current which passes from turn to turn of the secondary coil when over the primary, even if that secondary coil is open, and this dielectric current has the effect, in accordance with well-known principles, of reducing the effective inductance of the primary circuit. Nevertheless, in the above measurement it is proper to take as L the inductance of the primary measured in contiguity to the open secondary, and as the value of N the inductance of the secondary measured in contiguity to the open primary.

As an example of such a measurement the following figures may be given. A certain air-core transformer had a primary consisting of one turn of thick stranded copper wire, and a secondary of eight turns of thinner stranded wire. Measuring as above described, the following values in centimetres were found by the appliance here described:—

$L = 695$ cms., $N = 45{,}700$ cms.

$L_1 = L + 2M + N = 53{,}000$ cms.

$L_2 = L - 2M + N = 40{,}120$ „

Hence $M = \frac{1}{4}(L_1 - L_2) = 3{,}220$ cms.,

and $\frac{1}{2}(L_1 + L_2) = 46{,}560$ „

whilst from the independent measurements of L and N as above we have,

$$L + N = 46{,}385 \text{ cms.}$$

Hence, the agreement between the last two sums is fairly close. Also the coupling $M/\sqrt{LN}$ is found to be equal to 0·57.

It is usual to call the "coupling" of a primary and secondary coil "close" if it exceeds in value 0·5, and "loose" when it is less than 0·5.

The wave or frequency meter enables us to exhibit in the form of an attractive lecture experiment the well-known fact that the closing of the secondary circuit of an induction coil or transformer reduces the effective inductance of the primary coil. Also since it enables us to determine the frequency (n) of a high frequency current, and it enables us to determine also the value of the high frequency resistance R′ of a round sectioned copper wire of which the diameter d and steady or ordinary resistance R is known, since

$$R' = \frac{\pi d}{80}\sqrt{n} \,.\, R,$$

it becomes, therefore, a useful addition to laboratory appliances.

In Hertzian-wave telegraphy the varying power of waves of various lengths to travel over land or sea surfaces is well known, and it is, therefore, a practical necessity to be able to measure the wave-lengths of the wave sent out. The wave-meter enables us to conduct a kind of spectroscopy on a gigantic scale when we are operating with electric waves hundreds of feet in length instead of fractions of an inch.

We can by means of it discover, for instance, that a wave 300 feet in length travels well over a sea surface, but will not go across a city. On the other hand, the author has been able to communicate well across London by means of electric waves 1000 feet in wave-length.

[*Note added, February* 14, 1905.—The above-described instrument enables us to show that, in the case of an aërial wire or antenna, as used in wireless telegraphy, inductively coupled to a condenser exciting circuit, even if the two circuits, open and closed, have separately the same electrical time period, yet, when coupled, there are two waves radiated of different wave-lengths and frequencies, differing also in period from the free separate time period of each circuit. This result, predicted by theory, is confirmed by experiment.

A name is required by which to designate the instruments here described, and others of similar nature. The word wave-meter may probably be preferred in practice, but, if a special term is desired, the author suggests, with diffidence, the name *Cymometer* or *Kymometer* (from κῦμα, a wave) as applicable to it.*

"The Effects of Momentary Stresses in Metals." By BERTRAM HOPKINSON, M.A., Professor of Mechanism and Applied Mechanics in the University of Cambridge. Communicated by Professor EWING, F.R.S. Received January 31,—Read February 16, 1905.

In 1872 the late Dr. John Hopkinson published an investigation into the effect of a blow delivered by a falling weight on the lower and free end of a wire, the upper end of which is fixed.† It is unnecessary to repeat the mathematical analysis in full, but its main features appear in the following argument:—As soon as the weight strikes the stop at the lower end a wave of extension starts up the wire, and the velocity with which it is propagated is $\sqrt{E/\rho} = a$, where E is Young's modulus, and ρ the density of the wire. At a time t after the weight has struck, so short that its velocity is not appreciably diminished, the lower end of the wire has moved through a distance Vt, where V is the velocity of the weight immediately after striking. That is to say, the wire as a whole is lengthened by an amount Vt. This extension is felt over a distance at from the lower end, that being the distance through which the wave of extension initiated by the blow has travelled. The mean strain in this portion of the wire is therefore V/a, and the remainder of the wire is not extended. The wave now travels up the wire to the fixed end, and when it reaches there a reflected wave of equal amplitude starts down the wire. There results momentarily at the top end of the wire a strain equal to $2V/a$ with a corresponding tension $2EV/a$. This is the maximum tension experienced by any part of the wire until the reflected wave again reaches the lower end.

Each bit of the motion of the weight after striking contributes an element to the wave of extension, which is proportional to the then velocity of the weight. The weight is continually being retarded, and the amplitude of the wave therefore continually diminishes as you go back from its front.

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* The writer is indebted to his colleague, Professor A. Platt, for advice on the correct form of these words.

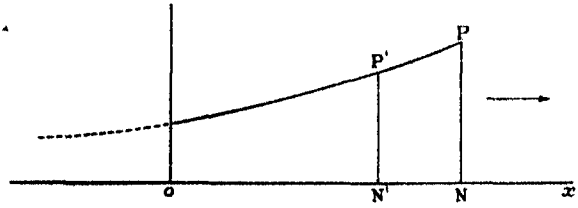
† 'Original Papers,' Hopkinson, vol. 2, p. 316.

In Fig. 1 the abscissæ are distances measured from O, the free end of the wire; the ordinates are the strains, and any one of them, say P′N′, is equal to v/a, where v is the velocity which the weight had when the bit of wave at P′ left it. If t be the time, reckoned from the moment of striking, ON = at, and it is easy to show that

$$\text{P}'\text{N}' = \text{PN}e^{-\frac{\mu\,.\,\text{NN}'}{\text{M}}} = \frac{\text{V}}{a}e^{-\frac{\mu}{\text{M}}(at-x)},$$

where μ is the mass of the wire per unit length, and M the mass of the weight. The wave of extension represented by the curve and its dotted continuation travels up the wire without change of type to the upper end, where it is reflected, and a similar wave travels down the wire, the effect of which is added to that of the original wave. The strain at any point of the wire, such as N′, is zero till the wave reaches it. The strain then becomes V/a, and gradually diminishes according to the exponential law $e^{-\mu at/\text{M}}$ until the reflected wave reaches N′, when the strain increases by V/a again. Further reflection will occur at the moving weight, but in my experiments this is not considerable, and the maximum strain experienced at any point of the wire, at any rate in the upper half, occurs when the reflected wave reaches it. If x' be the distance of the point from the *upper* end, the total strain due to the up-going and down-coming waves then is $(1+e^{-2\mu x'/\text{M}})\frac{\text{V}}{a}$. The movement in space of any point N′ before the reflected wave reaches it is equal to the area of the curve PNN′P′. For the point in question this is $\frac{\text{MV}}{\mu a}(1-e^{-2\mu x'/\text{M}})$. The strain caused by the blow is added to any initial strain in the wire. When, as is usually the case, the wire is under tension at the moment of the blow, and the tension is released by the blow, the initial strain in the wire is somewhat diminished by the time the wave reaches the top end; superposed upon the extension caused by the blow there is a slight contraction due to the release of the tension at the lower end at the moment of striking. The ultimate

FIG. 1.



result is that the total increase of length, caused by the blow, of a piece x' at the top end of the wire is

$$\frac{\mathrm{MV}}{\mu a}\left(1-e^{-\frac{2\mu x'}{\mathrm{M}}}\right)-\tfrac{1}{2}\frac{\mathrm{T}}{\mathrm{M}}\left(\frac{2x'}{a}\right)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where T is the initial tension. In my experiments $2\mu x'/\mathrm{M}$ is small, and its square may be neglected. The expression then becomes

$$2x'\frac{\mathrm{V}}{a}\left(1-\frac{\mu x'}{\mathrm{M}}\right)-\tfrac{1}{2}\frac{\mathrm{T}}{\mathrm{M}}\left(\frac{2x'}{a}\right)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2).$$

The second term is a small correction, but cannot in all cases be neglected. The piece of wire lengthens continuously as the wave passes over it, and begins to contract when the reflected wave arrives at its lower end. The extension then has the value given by expression (1). These results are all to be found in Dr. Hopkinson's papers cited above, or follow at once from the results there given; and so it does not seem necessary to repeat the proofs here.

In the same paper Dr. Hopkinson gave the result of some rough experiments which went to confirm the principal conclusion from this analysis, namely, that the power of a blow to rupture a wire should be measured rather by the velocity with which it is delivered than by its energy or its momentum. It also appeared, as might be expected, from the mathematics, that the wire was most likely to break at the upper end.

In these experiments, made over 30 years ago, the only available means of estimating the momentary stresses produced by the blow was the effect they left upon the wire, *e.g.*, rupture. As the mathematical treatment proceeds upon the assumption that the stress and strain are everywhere and always proportional, it was not to be expected that it could give more than a very general indication of the impulse necessary to rupture the wire. With the appliances now available, however, I think that experiments on these lines are capable of yielding a good deal of information about the effect of stresses applied for a very short time, such as are met with in most cases of shock. The practical importance of such information need not be insisted upon.

I have, therefore, made some experiments of the same kind, but instead of rupturing the wire I have used blows which leave but little permanent extension. I have measured the momentary extension of a few inches at the top of the wire, and compared this with the extension as calculated from theory and given in expression (1) above. If the two agree, and if not much permanent extension is left, it is clear that the theory is correctly applied, and that the stresses in the material may be calculated from it. Moreover, we know that the material must be substantially elastic up to the maximum stress so calculated if applied for the time given by the theory.

The general result that I have obtained is that iron and copper wires may be stressed much beyond the static elastic limit and even beyond their static breaking loads without the proportionality of stresses and strains being substantially departed from, provided that the time during which the stress exceeds the elastic limit is of the order of 1/1000 second or less.

The wire was in each case of No. 10 gauge, and about 30 feet long; it was hung in a vertical chase in a wall, the upper end being firmly fixed in a block of iron, weighing about 20 lbs., the ends of which were built into the wall. This block carried a vertical steel rod, at any point of which could be clamped the contact-making device for measuring the momentary extension. The construction of this sufficiently appears from the figure. The light hard steel point A is fixed to the wire at a certain distance, usually 20 inches, from the upper end. The wire having been drawn taut preparatory to the experiment, the insulated spring S is pushed up by the micrometer screw until contact is made with the point as shown by the deflection of the galvanometer. The spring is then withdrawn by the amount of extension expected; the blow is delivered and the galvanometer shows whether contact between the point and the spring has occurred or not.

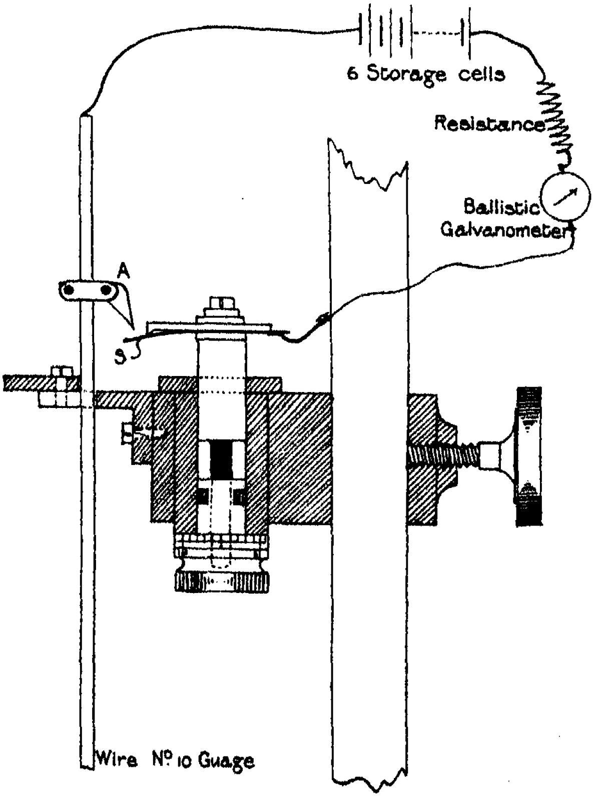
By using a sensitive ballistic galvanometer without any resistance in series with it, it was found quite easy to determine the instantaneous extension of 20 inches of wire correct to 1/1000 of an inch, that amount of difference in the position at which the spring is set converting a big throw of the galvanometer into no deflection at all. In a few cases a second point was added with a similar contact spring close to the upper end of the wire, in order that any displacement of the wire relative to its supports might be detected. But I found that if the wire was soft soldered into a bolt about 3 inches long screwed into the block, this precaution was unnecessary.

The falling weight was a cylindrical piece of steel weighing 1 lb., with a hole drilled along its axis which was a loose fit on the wire. The wire was kept taut by a spring balance attached to its lower end, the tension in which could be varied from 20 to 200 lbs. The stop struck by the falling weight was a metal sleeve slipped over the wire and soldered to the lower end. It was made as light as possible so that the velocity of the weight should not be much diminished at impact. The velocity at impact was calculated from the height of fall, being taken as $\frac{M}{M+m}\sqrt{2gh}$, where M is the mass of the weight, and m that of the stop.

From time to time the permanent extension on the 20 inches was measured by again pushing the spring into contact with the wire when under steady tension. No analyses were made of the materials, because, at the present stage, all that I desire to do is to compare the effects in the same material of impulsive and of long continued stress. The nature of the material, however, sufficiently appears from the static tests.

Iron Wire.—This was bought as iron wire, No. 10 gauge. Its diameter was 0·1275 inch. After placing it in the chase it was heated to redness and stretched, to straighten it. The annealing softened it materially, and somewhat unequally in different parts.

FIG. 2.



The following was a set of observations on this wire, which is typical:—

Steady tension 50 lbs.—Height of fall 5 feet.

Contact point 20 inches from the upper end.

One division on micrometer head = 1/2000 inch = 1/40000th part.

Micrometer reads 34·5 with a steady load of 50 lbs. when contact first made on the spring being pushed up.

Micrometer set at 110·5 (76 divisions extension). No contact when weight let fall.

Repeat the blow.—No contact. Repeat.—No contact.

Micrometer with steady load of 50 lbs. now reads 34·5.

Micrometer set at 109·5 (75 divisions extension). No contact.

Altered to 108·5. Contact occurred; the galvanometer spot went half across the scale.

Repeat.—Contact again.

Steady micrometer reading after this 36·0.

Micrometer set at 111 (75 divisions extension). No contact.

Repeat.—No contact. Repeat.—No contact.

Steady reading now 36·0.

Micrometer set at 110 (74 divisions extension). No contact.

Repeat.—Contact occurred.

Steady reading now 37·0.

Hence, the instantaneous extension in this case is 74 micrometer divisions, and the permanent extension produced by 11 blows is about 2·5 divisions.

Then followed a set of 4 blows with a 10-foot fall, and with 20 lbs. tension. They resulted as follows:—

Steady reading 7·0. Set at 110 (103 divisions). Contact.
Steady reading 20·0. Set at 125 (105 divisions). No contact.
Steady reading 29·5. Set at 132 (102½ divisions). Contact.
Steady reading 42·0. Set at 148 (106 divisions). No contact.
Steady reading 52·5.

Hence, the extension produced by the blow is probably between 103 and 105 divisions, and almost certainly between 102 and 106. Permanent extension produced by 4 blows = 45·5 divisions, or just over 1/1000th part.

Now static tests on this wire showed that a load of 390 lbs. extends it by 1/1000th part. Also μ its mass per foot is 0·0435 lb. Hence

$$a = \sqrt{\frac{E}{\mu}} = \sqrt{\frac{390,000 \times 32}{0{\cdot}0435}} = 17,000 \text{ f.s. nearly.}$$

The mass of the stop was 0·04 lb. Hence V, the velocity just after impact, is, with a 5-foot height of fall, 17·2 f.s. Also since $x' = 1{\cdot}66$ feet; $\frac{\mu x'}{M} = \frac{1{\cdot}66 \times 0{\cdot}0435}{1} = 0{\cdot}07$.

Further, $T = 50$ lbs. $= 1600$ poundals, and it will be found that $\frac{1}{2}\frac{T}{M}\left(\frac{2x'}{a}\right)^2$ is about 0·4 thousandth of an inch, or 0·8 micrometer division. Substituting these figures in the expression (2) above, the extension on the 20 inches, as calculated, is 37·2 thousandths of an inch, or, say, 74½ micrometer divisions. The observed extension is 74 divisions, which is close agreement. This, coupled with the fact that the permanent extension produced on the 20 inches is negligible, is fairly conclusive evidence that the theory is applicable in this case, and that the material is almost perfectly elastic up to the highest stress as calculated from the theory. The maximum strain at the top of the wire is $2V/a$, or $34 \cdot 4/17$ thousandths. The corresponding tension is about 790 lbs. To this must be added the 50 lbs. steady tension, making a total of 840 lbs. as the maximum stress experienced by any portion of the wire. The mean tension in the top 20 inches, where the extension is greatest, is $\left(\frac{74}{40,000} \times 390\right) + 50$, or 770 lbs.

Now, after the completion of the experiments, the top 20 inches of the wire were cut out and tested statically with a Ewing's extensometer. There was perceptible failure of elasticity at 500 lbs., very marked yielding at 700 lbs. (which produced a permanent extension of nearly 1 per cent.), and at 800 lbs. the wire drew out very rapidly and finally broke.

With a fall of 10 feet and a steady tension (T) of 20 lbs., the calculated extension will be found to be 53 thousandths of an inch, or 106 micrometer divisions. This, again, agrees very well with the observed extension of 104 divisions. In this case the calculated maximum tension at the top end is 1150 lbs., and the mean tension on the 20 inches about 1000 lbs. Of this extension, however, about 11 per cent. is permanent, so that there is some failure of elasticity, and it is improbable that the maximum stress quite reaches the calculated value. It is practically certain, however, that it exceeds the mean stress corresponding to the *elastic* part of the maximum extension in the top 20 inches, viz., about 900 lbs.

Next as regards the time for which these stresses are applied. The strain at the top of the wire is $2\frac{V}{a}e^{-\mu a t/M}$, where t is the time which has elapsed since the wire first arrived there. In the case of the 5-foot fall it will be found that the stress falls from 840 lbs., its initial and maximum value, to 500 lbs., which may be taken as the elastic limit, in about 0·8 thousandth of a second.

These results were fully confirmed by a large number of experiments in which different steady tensions were applied. The general conclusion is that in this material, which has an elastic limit of 40,000 lbs., or 17·8 tons per square inch, and breaks at 28·5 tons, a stress momentarily exceeding 75,000 lbs., or 33½ tons, and exceeding the static elastic limit for a time of the order of 1/1000 second, may be applied without any very great failure of elasticity.*

It may be further noted that a blow from a height of 10 feet, giving a tension momentarily exceeding 900 lbs., produces a permanent extension of 1/3500th part, or 1/30 of the ultimate extension caused by a steady load of 700 lbs.

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* The absolute stress is, as usual, calculated on the uncontracted area of the test-piece. The statical breaking stress at the moment of breaking is, of course, greater than this figure, but then the material is hardened by the drawing out.

Copper Wire.—This was 0·129 inch diameter, and of the kind used in electric light cables. It was set up without preparation of any kind. A load of 220 lbs. stretched it by 1/1000th part, corresponding to $E = 7500$ tons per square inch. The wire weighed 0·0503 lb. per foot. The steady tension was 200 lbs. Mass of falling weight (M) 0·945 lb.; mass of stop, 0·023 lb. Velocity of propagation of waves, a, $= 11,800$ f.s.

With a fall of 12·6 inches the additional extension observed on the top 20 inches was 41 micrometer divisions. The calculated extension (formula (2) above) is 43 divisions. The permanent extension produced by 20 blows was about 2 micrometer divisions.

With a fall of 2 feet 6 inches the observed extension was 67 divisions. The calculated extension is 70½ divisions. Ten such blows extend the 20 inches by 13·5 micrometer divisions, or 6·7 thousandths of an inch.

The elasticity is therefore practically perfect up to the stresses caused by a fall of 2 feet 6 inches. The greatest strain at the top end caused by this blow is $2V/a = 2{\cdot}10$ thousandths. The tension due to this is 440 lbs., and the resultant tension, including the initial 200 lbs., is 640 lbs. The mean tension on the top 20 inches is 570 lbs. (calculated from the observed extension of 67 divisions).

Tested statically with the extensometer, this wire showed failure of elasticity at 500 lbs. With a load of 590 lbs. it yielded rapidly and finally broke.

With a fall of 5 feet, and the same initial tension of 200 lbs., the observed extension on the top 20 inches was between 100 and 105 micrometer divisions, as against 103 calculated; of these about 30 divisions were permanent. The calculated maximum tension in this case (including the 200 lbs.) is 890 lbs. But the elasticity here is far from perfect, and the actual stress is probably somewhat less than the calculated value.

The observed extensions are, in the case of the copper wire, about 5 per cent. less than the calculated. I think that this is more than can be accounted for by errors of observation, or by such causes as friction between wire and weight, especially having regard to the much closer agreement in the other wires with which I have experimented. A possible explanation is that in the copper wire the value of Young's modulus for these extremely rapid extensions is 10 per cent. greater than for slowly applied forces. The difference between the adiabatic and isothermal elasticities as calculated from the coefficient of expansion and Young's modulus, is not sufficient to account for the effect, which must be a true time effect if it exists.

The history of the stress in a section of the wire after one of these blows is rather complicated, and it is difficult to deduce from the results anything more than the general conclusion stated above, that the wire is substantially elastic up to stresses much beyond the static elastic limit, and that the mathematical theory gives correct results. I hope, however, by suitable modifications of the experiment, to simplify the conditions, and obtain by this method more detailed information as to the properties of materials when subjected to shock. It seems to me quite possible that the stress-strain relations for stresses beyond the elastic limit may be much simplified if the stresses are applied for exceedingly short times, because the complication of hardening, due to overstraining, will be to a large extent removed.

"Phosphorescence caused by the Beta and Gamma Rays of Radium." By G. T. BEILBY. Communicated by Professor LARMOR, Sec. R.S. Received January 25,—Read February 9, 1905.

1. Various observers have noticed that barium platino-cyanide, after continued exposure to the rays from radium, becomes brown or red, while the phosphorescence excited by the rays falls off considerably.* The following observations were made with the object of ascertaining the conditions under which this change occurs.

2. A specimen of Merck's barium platino-cyanide was recrystallized and obtained in prisms from 3 to 5 mm. long. The crystals were bright canary yellow and showed a pale blue fluorescence by obliquely reflected light.

3. The radium used was 30 milligrammes of pure bromide contained in a cell with a thin mica cover. This radium is the property of Mr. Frederick Soddy, to whom I am much indebted for granting me its exclusive use for more than three months. All the experiments were made without removing the mica cover of the cell, so that the effects produced were due entirely to the β and γ rays. In comparing the phosphoresence at different stages, black paper was interposed between the cell and the substance so as to cut off the luminous rays from the radium.

4. When yellow crystals of platino-cyanide are left on the mica cover of the radium cell for half an hour, the beginnings of the colour change from yellow to red are distinctly visible. In one hour those surfaces most directly in the path of the rays become strongly reddened. In eight hours the phosphorescence has fallen to a minimum of 8/100 of its original amount, at which it remains, however long the exposure may be continued.

Crystals were exposed to the rays for eight days, but the phosphorescent value did not further diminish, though the colour became rather deeper.

5. When the reddened crystals are removed from the action of the rays they at once cease to phosphoresce. At the outset, therefore, there are two well-marked characteristics in the behaviour of the platino-cyanide. (1) The phosphorescence starts at a maximum value which rapidly falls to 1/12 or thereby; and (2) there is no after phosphorescence.

6. Other observers have stated that platino-cyanide screens which have been reddened by over-exposure to radium rays may be restored to the sensitive state by exposure to sunlight.* I have exposed reddened crystals on a glass plate to a condensed beam of sunlight for several hours without being able to observe any restoration of colour or phosphorescent quality. The observations here recorded seem to suggest that the restorative effect of sunlight, where it has been observed, must have been due to some conditions supplied by the other materials of which the screen was composed. The present observations show that the red crystals retain their new character over a period of many weeks either in the dark or in diffused daylight, and none of these observations have given any indication that the change is other than permanent.

7. The only way *completely* to restore the red crystals to the yellow state is by solution in water and recrystallisation. The properties of the crystals obtained in this way appear to be in all respects the same as they were before exposure to the rays. It would appear, therefore, that the reduction of the phosphorescent value is not primarily due to chemical change in the salt.

The fully developed crystalline condition of the yellow salt is evidently necessary, if the highest phosphorescence is to be obtained. Anything, therefore, which interferes with this condition impairs the phosphorescence.

8. When the water of crystallisation is wholly or partially expelled, the crystals, either yellow or red, are left in the form of an amorphous powder of a brick red colour. In this amorphous state the value of the phosphorescence has fallen to 2/100 and the colour of the glow is no longer green but red. As crystals reddened by exposure to the β rays lose water and become opaque on heating to 130° just as the yellow crystals do, it may be concluded that the change from yellow to red under the influence of the β rays is not due to the loss of water of crystallisation.

9. As the reduction of the phosphorescent value in the change from the yellow to the red form is neither due to chemical decomposition nor to loss of water of crystallisation, it occurred to me that it might be akin to the change from the crystalline to the amorphous state,

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* Rutherford, 'Radio-activity,' p. 168.

which had been observed in metals and other solids when they are flowed by mechanical movement.[*] The falling off of the phosphoresence under the long continued action of the rays suggested a failure in elasticity or elastic response analogous to that which is known in metals as "elastic fatigue," while the colour changes appear to be of the same nature as those observed in the crystalline and amorphous phases of the metals.[†]

10. When a small fragment of a yellow crystal is bruised on a glass plate by the rounded end of an agate pestle, the bright yellow colour is changed to deep red-brown wherever the pressure has acted so as to cause flow. This colour change is remarkably sharp and distinct. By rolling the pestle firmly over the smaller crystalline specks these are completely flowed into transparent patches with smooth rounded outlines. The colour of the thinnest patches is obviously more intense, as well as much redder, than that of the original crystal, while the thicker patches are of a very intense red-brown by transmitted light. The colour of the flowed patches by reflected light is complementary to that by transmitted light, being green. The crystalline structure of the yellow salt is to all appearance completely replaced by the vitreous granular structure of the amorphous phase.

11. A small quantity of the amorphous platino-cyanide was prepared by bruising and flowing the yellow crystals on a glass plate. With each portion the operation was repeated several times, that is to say, the flowed patches on the plate were scraped off, broken up and again rolled with the pestle. In this way, a fairly complete conversion into the amorphous form was obtained. The final product consisted partly of brown powder and partly of deep brown scales with a greenish sheen. The phosphoresence in the β rays was reduced to 2/100 of its value, and it appeared as a dull red glow in which an occasional speck of bright green indicated the presence of minute portions of the untransformed crystalline phase.

12. In my earlier observations on the phase changes $A \rightleftarrows C$[‡] it was shown that while the transformation $C \longrightarrow A$ takes place by mechanical movement of the molecules over each other, as in a liquid, the reverse transformation $A \longrightarrow C$ takes place only when a definite transition temperature or stability point is reached. The low temperature at which platino-cyanide loses its water of crystallisation presented a difficulty in attempting to bring about the transformation $A \longrightarrow C$ by heat, but an encouraging result was obtained on quickly raising a small portion of the amorphous salt to 85°, for the dark brown scales immediately assumed the bright greenish yellow of the

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[*] 'Phil. Mag.,' vol. 8, 1904, pp. 258—276.

[†] *Ibid.*, also 'Roy. Soc. Proc.,' vol. 72, pp. 218—235.

[‡] *Loc. cit.*

crystalline phase. The reality of this change was further confirmed by finding that the phosphorescent quality, which had fallen to 2/100 in the amorphous state, had been restored by the heating to 33/100.

13. The analogy between the changes in colour and phosphorescent quality brought about by the transformation C ——→ A and the corresponding changes which result from the action of the β rays is thus shown to be very close; it remained to be seen if the analogy also held good in the reverse transformation by heat.

14. Crystals which had been reddened by the β rays were lightly crushed and quickly heated to 110° in a capillary tube with an open end. The colour of the salt became much paler and its phosphorescent quality was considerably increased. As the temperature necessary to bring about the transformation was also high enough to drive off some of the water of crystallisation, a fresh portion of lightly crushed red crystals was packed tightly into a capillary tube which was sealed off as close to the surface of the salt as possible. The tube was heated to 120°, when the transformation into the yellow salt took place quite sharply, beginning simultaneously at the middle and at one end of the tube and quickly spreading all over, the brown colour giving place to bright yellow. The transformation was carried out at 120°, so that no water in the liquid state can have taken part in it. After cooling, some minute drops of condensed water were visible on the inner surface of the tube. Necessarily, a corresponding portion of the salt must have parted with some of its water of crystallisation, but this did not affect the transformation of the remaining part. The phosphorescent quality was raised from the 8/100 of the red crystals to 33/100.

15. Even in the sealed tube, however, the conditions for the transformation A ——→ C are distinctly unfavourable to anything like a perfect conversion or the production of a uniformly crystalline material, therefore, the very definite results obtained, namely, the partial restoration both of colour and phosphorescence, are strongly confirmatory of the phase view of the change brought about by the β rays.

16. The retention by the reddened crystals of their crystalline form and transparence points to a persistence of a proportion of the crystalline phase side by side with the amorphous. Having regard to my earlier observations on phase transformation in overstrained crystals, this persistence of the C phase is quite to be expected. In the case of gold it was shown that even after severe and repeated beating of the metal in the form of the thinnest foil the crystalline structure could not be completely obliterated.* More recent observations on the flow of crystalline salts, which have not yet been published, fully confirm this point. These still further confirm the explanation of this fact offered in my former papers, namely, that the amorphous phase which is formed at all the moving surfaces of the crystalline units acts as an

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* 'Phil. Mag.,' vol. 8, p. 263.

encasing medium which protects the crystalline elements from further disintegration. In the case of the platino-cyanide, the over-stimulation to which the vibrating molecules are subjected by the β rays during the preliminary stage of bright phosphorescence, results in a state analogous to that of elastic fatigue in vibrating metal wires or glass fibres. Up to a certain point this fatigue may be recovered from, that is to say, if the relative displacements of the molecules from their proper crystalline relations has not passed beyond a certain stage; but beyond this stage there is no power of self-recovery, and heat is required to endow the molecules with freedom of movement sufficient to enable them to return to their crystalline positions. This final stage of permanent fatigue or overstrain in the salt corresponds with the amorphous condition which results from mechanically produced flow.

17. The foregoing observations show that physical structure and molecular elasticity may play an important part in the initial stimulation of phosphorescence, but the persistence of phosphorescence, even in the purely amorphous form of the substance, seems to point to the necessity for a more general explanation of the phenomena of phosphorescence. I propose to deal with the more general aspects of the subject in a separate communication.

18. In the appended table the comparative phosphorescence of the various forms of platino-cyanide of barium is shown. The method used was to measure the distance from the radium at which the salt exposed on a tray of black paper became distinctly visible in the dark. The salt was observed by means of a simple microscope fixed over the tray. The intensity of the rays was taken to be inversely as the square of the distance of the radium from the phosphorescing salt.

Comparative Phosphorescence (that of the canary-yellow crystals being taken as 100).

	Phosphorescent value.	Reference to paragraph.
1. Yellow crystals	100	No. 2
2. " " after exposure to β rays for 8 hours....	8	" 4
3. The same for 44 hours	8	" 4
4. Red crystals (No. 3 above) after heating to 110° in open tube	27	" 14
5. Red crystals, after heating to 120° in sealed tube	33	" 15
6. Yellow crystals dehydrated at 180° ...	2	" 8
7. Yellow crystals flowed into amorphous scales	2	" 11
8. The same (No. 7) heated to 85°—100°	33	" 12

"Phosphorescence caused by the Beta and Gamma Rays of Radium.—Part II." By G. T. Beilby. Communicated by Professor J. Larmor, Sec. R.S. Received February 9,—Read February 23, 1905.

19. By the study of the case of barium platino-cyanide, it has been shown that certain forms of phosphorescence or luminescence are due to change of physical state—*e.g.*, to the passage from the crystalline to the amorphous state, or from one amorphous state to another. The molecular movement required to bring about these changes may be caused—(1) by disintegration produced by mechanical means, as in the crushing or flowing of crystals; (2) by the expulsion of a volatile constituent, as in the dehydration of crystals, the molecular movement which necessarily occurs at the moment of expulsion being taken advantage of by the forces of cohesion to establish new arrangements of the molecules either crystalline or amorphous; and (3) by a condition of excessive vibration and ultimate overstrain set up by a stream of electrons, as in the radium or the cathode rays.

20. After due allowance has been made for the element of physical change, there remains a large class of phosphorescent phenomena which cannot be thus explained; but I believe that the clear recognition of the part played by physical change at once makes the consideration of the latter class much simpler.

21. Even in the case of platino-cyanide, where it is seen that physical changes play so large a part in the phosphorescent phenomena, there remains a certain residuum of phosphorescent effect which appears to be independent of the physical condition of the substance. Platino-cyanide itself, therefore, opens the way to a further study of the phenomena of phosphorescence; but other substances in which the physical state plays a less important part are better suited for this study.

22. Throughout this paper the different phases of luminescence are referred to as: *primary phosphorescence*, or the luminescence produced under the direct influence of a stimulus, *e.g.*, the β rays or the cathode rays; *secondary phosphorescence*, or the luminescence which continues after the direct stimulation has ceased; *revived phosphorescence*, or the luminescence revived by heat after the secondary phosphorescence has diminished or ceased altogether.

23. It has been shown that primary phosphorescence is exhibited under various forms of stimulation and under conditions in which the elastic vibration of molecules or molecular aggregates might alone account for the generation of light waves. But when the secondary and the revived forms of phosphorescence appear, it becomes necessary to suppose that these effects are due to some more intimate changes among the atoms themselves; in other words, to the play of chemical

affinity. The association of phosphorescence with certain forms of slow oxidation was early recognised, and possibly for this reason there has sometimes been a tendency to limit the chemical view to this type of action. But from the observations which follow it will be seen that with many substances the chemical actions which occur must necessarily be self-contained and independent of atmospheric or other surroundings.

24. The chemical action of the rays from radio-active substances has been recognised from the first. Among the most prominent examples of this action are—the reduction of sensitive silver salts in photographic films which led to the original discovery of the rays by M. Becquerel; the coloration of glass, first observed by M. and Madame Curie, and afterwards attributed by Elster and Geitel and other observers to the reduction and separation of the alkali metals in a state of solid solution; the electrolysis of water; and the separation of iodine from iodoform, observed by W. B. Hardy and Miss Willcox in the liquid state, and more recently by van Aubel in the solid state. Some of these actions have been recognised by direct chemical tests, while others have been inferred from the colour changes occurring in the substances exposed to the rays.

25. So far as I can learn, no systematic attempt has yet been made to trace the connection between the chemical, the coloration, and the luminescent effects of the β rays. The observations which follow are to some extent a repetition of the experiments of previous workers on the subject, but they have been extended in particular directions with the express object of throwing light on the problems of secondary and revived phosphorescence.

In these observations, as in those recorded in the first part of the paper, the substances under examination were exposed to the β and γ rays only (see paragraph 3).

26. A polished lens of rock crystal, after exposure to the rays for four days, showed a patch of dark brown coloration at the spot where the rays had entered. On removal from the radium, the coloured patch phosphoresced faintly. This could only be seen in complete darkness. After an interval of six weeks the lens showed no trace of phosphorescence at the ordinary temperature, but on heating it on a hot plate to rather over 100° the coloured patch glowed so brightly that it lighted up the rough edges of the lens and showed its complete outline quite distinctly. On raising the lens to a considerably higher temperature, probably over 250°, it glowed more brightly, and then the glow ceased altogether. The brown coloration had now completely disappeared.

27. A colourless crystal of calcspar, measuring roughly 17 × 12 × 6 mm., was exposed to the rays for six days. A faint yellow coloration marked the spot where the rays had entered. The coloration had penetrated about 2 mm. below the surface. When the crystal was first

placed on the radium cell it phosphoresced with a pale greenish light; but after a few minutes the spot at which the rays entered glowed with an orange red phosphorescence. This glow rose to a certain pitch, and then continued fairly uniform throughout the exposure to the rays. On removal from the radium at the end of six days the crystal continued to phosphoresce as brightly as it had done in the path of the rays. Twenty-four hours later the crystal still phosphoresced, though less brightly. On warming it to 80° the glow became brighter than it had originally been. On cooling again to the ordinary temperature the glow was feebler than it had been before heating. The reserves of phosphorescing power had evidently been more quickly expended at the higher temperature.

28. The gradual disappearance of the phosphorescence was watched day by day for a week. Four days after removal from the radium the crystal could still be seen in complete darkness. Heated to over 100°, the phosphorescence was much augmented, but the glow was distinctly whiter than it had originally been. Five days after removal from the radium the crystal had become quite invisible in complete darkness, but on heating it to over 100° it again phosphoresced. On the sixth day it still phosphoresced feebly when heated to 100°, but on raising it to 150° it glowed so brightly that it could be seen distinctly in a dimly lighted room. The phosphorescence was now even whiter and more diffused than it had been before. On the fifth day the patch of yellow coloration had completely disappeared. This disappearance coincided with the loss of phosphorescence at the ordinary temperature and also with the development of the whiter and more diffuse glow when the crystal was heated. On the seventh day the crystal heated to 150° gave a feeble white phosphorescence. On this occasion a crystal of calcspar, which had not been exposed to the radium, was heated side by side with the other which had. This fresh crystal gave absolutely no phosphorescence at 150°.

29. A piece of potash glass exposed to the rays showed a feeble fluorescence. After 60 hours it was removed from the radium. Where the rays had entered the surface, a strong brown coloration had taken place. This coloured patch phosphoresced feebly. Six weeks later the glass was examined and showed no phosphorescence at the ordinary temperature, but on heating to 100° it gave a faint greenish glow. The depth of colour of the brown patch in the glass showed no diminution of intensity at the ordinary temperature with the lapse of time, but on heating to about 200° the coloration completely disappeared.

30. A lens of colourless flint glass, tested for lead by heating one of its edges to the softening point in a gas flame, showed the usual brown coloration of lead glass. The lens was placed on the radium cell and at once phosphoresced feebly. After 12 hours' exposure to

the β rays, it showed no secondary phosphorescence on removal from the cell, and no revived phosphorescence when it was heated to about 200°. A brown coloration, which had resulted from the action of the rays, had completely disappeared after the heating to 200°. After a further exposure of 48 hours to the β rays, the brown coloration was much stronger, but it showed neither secondary nor revived phosphorescence.

31. A crystal of potassium iodide placed on the radium cell phosphoresced faintly. After three hours' exposure the phosphorescence was distinctly stronger, and on removal from the rays a faint secondary phosphorescence could be detected. This died out in a few minutes, but was revived for a few minutes on heating the crystal to 150°. After 12 hours' exposure to the rays, a faint blue-green colour had developed, which, however, disappeared after the crystal had been kept in the dark for a few hours.

32. A crystal of potassium chloride became red-purple after it had been two hours on the radium cell; during the exposure it phosphoresced faintly. On removal from the rays it gave a faint and brief secondary phosphorescence and a brighter revived phosphorescence on heating to 100°. After heating, the purple colour had disappeared.

33. A crystal of potassium bromide, after exposure for one hour, became blue-green and phosphoresced brightly. On removal from the rays it phosphoresced strongly, and on heating to 100°, it glowed with revived phosphorescence and lost its blue-green colour.

These potassium salts show the same association of colour with luminescence as calcspar, quartz, and glass, but all the effects are of a more evanescent character.

34. A crystal of potassium chloride was crushed and then flowed into amorphous scales. The scales when placed on the radium cell phosphoresced faintly, and in 30 minutes were tinted with a red-violet. In six hours the colour had deepened. On removal from the rays there was secondary phosphorescence, but both this and the colour disappeared more quickly than had been the case with the more massive crystal.

35. A small crystal of calcspar was crushed and then flowed into amorphous scales. The scales were placed on the radium cell. They phosphoresced very faintly, and there was no obvious increase over a period of three hours' exposure. Removed from the rays there was faint secondary phosphorescence, and when heated to rather below 100° they glowed with a bright orange phosphorescence and continued to do so for some minutes.

36. In the last two observations, after making due allowance for the small quantities employed and their fine state of division, it appears that the fact of a substance being in the amorphous instead

of the crystalline condition does not necessarily interfere with the generation and storage of energy which can afterwards be set free by heat and give rise to revived phosphorescence.

37. In the foregoing observations the coloration effects have, with one exception, been directly associated with the luminescent appearances (paragraph 30). The one exception is valuable, however, because it draws attention to the fact that the intensity of the affinities of the dissociated ions, as well as their suitable insulation, is a necessary factor in the production of phosphorescence. The lead silicate is easily electrolysed, and its ions are duly insulated as shown by the coloration; but in their recombination the energy developed in this particular case was insufficient to develop visible light waves.

38. In the haloid salts of potassium the conditions are entirely different, for the affinity of the haloid and the metallic ions is so intense that the insulating power of the molecules is only sufficient at ordinary temperatures to keep them apart for a very short time. It appears probable that in these salts so much energy might be stored by the action of the rays at a low temperature as would result in a most brilliant luminescence on a return to the ordinary temperature.

39. Another feature brought out by the foregoing observations is the remarkable persistence of latent phosphorescence as shown by the indefinitely long time for which this storage of energy can take place under favourable conditions (see paragraphs 26 and 29).

40. In tracing the various steps in the action of the rays as disclosed by the intensity and colour of the phosphorescence and by the appearance and disappearance of coloration, the chemical or electrolytic hypothesis seems to explain each step in a satisfactory way and without any straining of the facts. When the rays are first applied there may be a preliminary stage during which the luminescence is mainly of physical origin. This is borne out by the undoubted influence of crystalline structure on primary phosphorescence and its relatively small influence on the later stages of luminescence. But as electrolytic dissociation proceeds, a point is reached when the neutral molecules are no longer able to keep the increasing number of ions apart. Recombination then sets in, and with it the production of a new kind of luminescence. When once the insulating power of any given layer of the substance is saturated, the number of ions dissociated at each moment will be balanced by the recombination of a like number. This is the probable explanation of the fact that the phosphorescence reaches a steady value after a certain time. When this steady state has been reached for the whole depth to which the electrons can penetrate, the limit of storage of energy for the production of secondary and revived phosphorescence has been reached.

41. When the stimulus of the rays is removed, electrolytic dissociation will cease, but a certain number of ions continue to find their way to each other and to combine, producing secondary phosphorescence. This state may last only for a moment or it may continue for days (paragraph 28). The insulating power of the molecules depends on their mobility, and this in turn depends on temperature. For every rise in temperature a new equilibrium point must be established, and a further combination of ions with a fresh outburst of luminescence will occur. At whatever stage a rise of temperature takes place, the effect must be the same, whether it be at the first stage while dissociation is active, at the second stage while recombination is taking place, or at the third stage when equilibrium at the lower temperature had been reached and luminescence had entirely ceased.

42. From this point of view it becomes possible to explain the comparatively conflicting observations on the behaviour of the same substance in the cathode rays or in the radium rays. To take only one example of this: In 1881* Sir W. Crookes stated that calcite showed the residual glow longer than any substance he had experimented with. "After the current has been turned off the crystals shine in the dark with a yellow light for more than a minute." This short period of secondary phosphorescence as compared with the four days recorded in paragraph 28 becomes perfectly intelligible when the temperature is taken into account. No mention of the actual temperature is made in Crookes' observation, but it may fairly be assumed that the temperature of a substance exposed to a powerful cathode discharge would be very much raised. Even a temperature of 100° would break down the insulation of the calcite molecules to such an extent that only a very brief secondary phosphorescence could occur.

43. The effects of low temperature in developing and increasing secondary phosphorescence, as shown by Crookes and Dewar, fall naturally in line with the dissociation hypothesis. By the increased insulating power of the molecules at the lower temperature the capacity of a substance to store dissociated ions may be increased to an enormous extent, so that the break-down of insulation by a rapid return to the ordinary temperature will set free a great store of energy and produce an outburst of phosphorescence. It is evident that substances which have too little insulating power at ordinary temperatures to enable them to produce secondary phosphorescence may at the lower temperatures develop this power to a high degree. Even the much feebler stimulus of the light waves may thus be enabled to record dissociation effects which have altogether escaped notice at ordinary temperatures.

44. The conclusions drawn in the foregoing papers may be briefly summarised under the following divisions:—

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* 'Chem. News,' 1881, p. 287.

1. Certain types of phosphorescence are due to the molecular movement or displacement which is produced by heat, by mechanically applied stresses, or by radiant energy.

2. Certain other types of phosphorescence are distinguished by their appearance in three stages, called here primary, secondary, and revived phosphorescence. These can be explained as due to atomic changes in which chemical affinity is the controlling factor.

3. The phenomena of this type appear to support the view that a species of electrolysis occurs in solids exposed to the β or cathode rays; that the products of electrolytic dissociation are insulated or partly insulated from each other by the neutral molecules, as in a viscous electrolyte; and that it is the breaking-down of this insulation and the recombination of the ions which causes revived phosphorescence.

[*Added February* 22, 1905.—The following experiments have been made at a temperature of about $-100°$:—

44. Calcspar crushed to powder, and exposed to the radium rays for an hour at this temperature, showed the usual primary and secondary phosphorescence. On emptying the salt from the cold tube upon a metal plate at the ordinary temperature, the glow increased considerably as the temperature of the salt rose; but this revived phosphorescence was not so vivid as that observed between 15° and 100° (see paragraph 35).

45. Potassium chloride exposed to the rays for an hour at $-100°$ showed well-marked violet coloration. The primary and secondary phosphorescence were brighter than at the ordinary temperature (see paragraph 32). When the cooled salt was emptied on the metal plate it glowed with a brilliant pink phosphorescence, which died down in less than a minute. On returning the salt to the cold tube, the phosphorescence completely ceased.

46. Potassium bromide treated in the same way was coloured greenish blue in one and a half hours. It showed distinct primary, but no secondary, phosphorescence. Emptied on the metal plate, it glowed with a brilliant greenish phosphorescence, which quickly died down, and entirely ceased when the salt was returned to the cold tube (see paragraph 33).

47. Barium platino-cyanide in yellow crystals exposed to the rays at $-100°$ turned red more slowly than at the ordinary temperature. After five hours' exposure the primary phosphorescence had fallen to 33 per cent. of its former value. There was still no secondary phosphorescence, but, when emptied on the metal plate, the salt glowed brilliantly for a few seconds. To make sure that this revived phosphorescence was not due to the purely physical effect of cooling and heating, another portion of yellow crystals was cooled under identical conditions, except that the radium was absent. The crystals

showed no phosphorescence of any kind even on the metal plate (compare paragraphs 4 and 5, Part I).

48. These observations at − 100° confirm the view (paragraph 38) that the effect of low temperature is to increase the insulating power of the molecules, and thereby to enable some substances to store chemical energy which are unable to do so at all at higher temperatures, *e.g.*, barium platino cyanide; and to increase the storage capacity of other substances in which the secondary phosphorescence is very short-lived at higher temperatures, *e.g.*, potassium chloride and bromide. In the case of calcspar, the insulating capacity at ordinary temperatures is already so excellent, as shown by the persistence of secondary phosphorescence, that there is comparatively little gain at the lower temperature.

49. If, as seems most probable, the coloration of solids by the β rays is due to the presence of ions, it is interesting to note that the different salts of potassium give perfectly distinct colours, the chloride being a red violet and the bromide and iodide a greenish blue. This difference is most likely due to the modification of the colour of the potassium ions by the presence of the haloid ions, chlorine, bromine, or iodine.]

"Note on the Determination of the Volume Elasticity of Elastic Solids."*

By C. CHREE, Sc.D., LL.D., F.R.S. Received December 21, 1904,—Read February 2, 1905.

In a recent paper† Mr. A. Mallock gives an ingenious and simple method of determining the coefficient of volume elasticity (bulk modulus) of metals by direct observation of the extension of a hollow right circular cylinder under uniform internal pressure.

The method depends on a result of the mathematical theory which seems capable of being proved in a more direct and complete way, but which at the same time requires to be restricted by conditions to which Mr. Mallock does not seem to refer. Further, the method is only one of several which seem equally worthy of consideration.

When dealing with isotropic material I shall employ the following notation:—

$$\mathrm{E} = \text{Young's modulus}, \qquad \eta = \text{Poisson's ratio},$$

$$k \equiv \tfrac{1}{3}\mathrm{E}/(1-2\eta) = \text{bulk modulus}.$$

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* [The main results of the first part of this paper (Case *i*) were worked out as a verification before Mr. Mallock's paper was printed; they were considered to have been sufficiently indicated in a footnote appended to the paper.—J. L.]

† 'Roy. Soc. Proc.,' vol. 74, p. 50.

Also l will denote the length of the whole or a part of a generator of a right cylinder or prism, δl its elastic extension.

When a hollow tube of isotropic material, bounded by co-axial right circular cylinders, is exposed to uniform pressures, viz., p_i over the inner surface, radius r_1, and p_e over the outer surface, radius r_2, and to uniform tension P over the flat ends, the elastic displacement parallel to the length, taken as axis of z, is given by

$$w = z\left\{\frac{\mathrm{P}}{\mathrm{E}} - \frac{2\eta}{\mathrm{E}}\,\frac{r_1^2 p_i - r_2^2 p_e}{r_2^2 - r_1^2}\right\} \qquad (1).^*$$

Case (i).—

$$p_e = 0, \quad \mathrm{P} = p_i r_1^2/(r_2^2 - r_1^2) \qquad (2),$$

$$\frac{\delta l}{l} = \frac{w}{z} = p_i \frac{r_1^2}{r_2^2 - r_1^2}\,\frac{1 - 2\eta}{\mathrm{E}} = \frac{p_i r_1^2}{r_2^2 - r_1^2}\,\frac{1}{3k} \qquad (3).$$

Putting for shortness

$$\delta l/l = \epsilon, \qquad r_2 - r_1 = t,$$

we have

$$k = \frac{p_i r_1}{3t\epsilon}\,\frac{r_1}{r_2 + r_1} \qquad (4).$$

When the thickness, t, of the cylinder wall is so small that t/r_1 is negligible compared to unity,

$$k = p_i r_1/6t\epsilon \qquad (5).$$

Case (ii).—

$$p_i = 0, \quad \mathrm{P} = -p_e r_2^2/(r_2^2 - r_1^2) \qquad (6),$$

$$\frac{\delta l}{l} = \frac{w}{z} = -p_e \frac{r_2^2}{r_2^2 - r_1^2}\,\frac{1}{3k} \qquad (7).$$

Thus, with the same notation as in Case (i),

$$k = -\frac{p_e r_2}{3t\epsilon}\,\frac{r_2}{r_2 + r_1} \qquad (8).$$

When t/r_2 is negligible compared to unity,

$$k = -p_e r_2/6t\epsilon \qquad (9).$$

Case (iii).—

$$p_i = p_e = -\mathrm{P} = p \qquad (10).$$

$$\delta l/l = w/z = -p/3k \qquad (11),^\dagger$$

and so

$$k = -p/3\epsilon \qquad (12).$$

Case (i) is really that considered by Mr. Mallock. Taking a cylindrical tube with terminal caps, he applies a uniform internal pressure p_i. This gives on each cap an outwardly directed pressure, whose total amount is $\pi r_1^2 p_i$. This leads to a longitudinal tension in the cylinder wall. Denoting the mean value of this tension per unit area by P, we have, since the cross-section of the material is $\pi(r_2^2 - r_1^2)$,

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* 'Amer. Math. Soc. Bull.,' 2nd series, vol. 7, 1900, p. 141.

† *Cf.* 'Phil. Mag.,' December, 1901, Eqn. (67), p. 594.

$$P\pi(r_2^2 - r_1^2) = p_i\pi r_1^2, \quad \text{or} \quad P = p_i r_1^2/(r_2^2 - r_1^2).$$

The first limitation above referred to is this: The longitudinal tension exerted on the cylindrical wall by the terminal caps will not in reality be uniformly distributed over the terminal areas $\pi(r_2^2 - r_1^2)$; thus the solution is reliable only when the principle of equipollent systems of loading* is applicable. This means that portions of the tube near the ends should be excluded from the solution, the portions being shorter the thinner the cylindrical wall.

The second limitation is that Mr. Mallock starts by assuming the tube wall very thin, and arrives at a formula which is presumably (5), and which at all events possesses the same limitations.† The formula is applied, however, by Mr. Mallock on his p. 52 to cases in which t/r_1 varies from about 1/19 to 1/5. The application of (5) under the circumstances would mean an error of from $2\frac{1}{2}$ to 10 per cent. in the value of k.

Case (ii) is parallel in every respect to Case (i) and would apply,

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* Todhunter and Pearson's 'History of Elasticity,' vol. 2, Arts. [8], etc.

† The primary formula, to which Mr. Mallock's calculations seem to lead him, as given on his p. 51, is

$$\kappa_x = Pr/2te_x,$$

from which he apparently derives $\kappa = Pr_2/6te$.

P represents the internal pressure. I do not follow Mr. Mallock's proof of the formulæ. But his κ and e must, I think, be respectively equivalent to k and ϵ of the present paper.

An attempt to ascertain the true significance of Mr. Mallock's r_2 from the numerical results on his p. 52, seemed to show that some errors of calculation must exist, independently of the precise meaning of r_2. It thus appeared desirable to recalculate the results from the exact formula (4). They appear in the following table, alongside of the values given by Mr. Mallock. The pressure applied was in all cases "400 lbs. per square inch."

Material.	l.	Outside diameter.	t.	State of material.	$\delta l \times 10^3$.	$10^{-11} \times k$ in C.G.S. units.	
						Mallock.	By (4).
	in.	in.	in.		in.		
Steel	60	0·75	0·0190	Hard	2·8	18·4	18·0
				Annealed	2·75	18·2	18·3
Brass....	50	0·415	0·0185	Hard	2·12	11·05	10·6
				Annealed	2·09	10·75	10·7
Copper ..	50	0·4485	0·0382	Hard	0·562	28	18·1
				Annealed	0·71	16·2	14·3

There is an obvious omission of decimals in Mr. Mallock's values for brass, which has been corrected above.

under similar limitations, to a cylindrical tube closed by caps and exposed to uniform external pressure p_e. The tube exposed to pressure would have to be contained in a strong vessel, having a glass roof or side. This might present disadvantages, but the test tube itself would be less exposed to temperature changes than in Case (i) and might be of a very simple type; so that once the containing vessel was built experiments on a variety of materials would be simple.

Case (iii) is only a special instance of the obvious result that when an isotropic solid of any shape, bounded by any number of surfaces, is exposed to pressure p, the same at every point of each and all of its bounding surfaces, *every* line in it whose original length is l suffers a shortening given by $\delta l/l = -p/3k$.

In Case (iii) any body will serve the purpose, but a long rod would be the natural form to adopt. This means a simpler test object than in Cases (i) and (ii), and there is the further recommendation that the mathematical solution is exact right up to the extremities of the object. The compensating disadvantage is that it requires a very long test object, or a very high pressure, to give sufficient extension, unless extremely refined methods of measurement exist. In Cases (i) and (ii) by using a thin walled tube one has much greater sensitiveness.

By subjecting a cylindrical tube successively to internal and external pressures, and determining values for k by both the methods (i) and (ii), interesting information could be obtained as to whether the bulk modulus is or is not the same for extension and compression. Removing the caps, and determining E by simple longitudinal tension, one would thus determine fully the elastic properties of the material, assuming it isotropic.

In any case δl should be measured from the equilibrium position of the test object after it is supported, and if it is hollow and exposed to internal fluid pressure after it has been filled with liquid.

Results in some respects more general than the preceding are obtained very simply from the formulæ which I have given for the mean change of length in elastic solids under any given system of loading.

Not confining ourselves to isotropy, suppose first that the material is merely symmetrical with respect to three rectangular planes, which we may suppose perpendicular to the axes of x, y and z.

Let E_3 be Young's modulus for traction parallel to the axis of z, and η_{31}, that one of the (six) Poisson's ratios which answers to traction parallel to z and contraction (strain) parallel to x.

Let $g \equiv d\gamma/dz$ represent the extensional strain parallel to z. Then in a body of any shape exposed to surface forces whose components at any point parallel to x, y, and z are denoted by F, G, H, the mean value $\bar{g}$ of g throughout the whole volume v is given by

$$E_3 v\bar{g} = \iint (Hz - \eta_{31}Fx - \eta_{32}Gy)\, dS \quad \ldots\ldots\ldots\ldots \quad (13).^*$$

Confining ourselves to the case where the material is symmetrical, about $0z$, we have

$$\left.\begin{array}{ll} \eta_{31} = \eta_{32} = \eta, \text{ say}, & \eta_{12} = \eta_{21} = \eta', \\ \eta_{13} = \eta_{23} = \eta'', \text{ say}, & E_2 = E_1 = E' \end{array}\right\} \ldots\ldots\ldots \quad (14).$$

Also, writing E for E_3 it may be shown that

$$\eta''/E' = \eta/E \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (15).$$

Suppose, now, the solid to be a hollow right prism exposed to uniform tension P over its flat ends, S, and to uniform pressures, p_i over its inner surface S_i, and p_e over its outer surface S_e, then

$$Ev\bar{g} = \iint PzdS + \eta \iint p_i(\lambda_i x + \mu_i y)\, dS_i + \eta \iint p_e(\lambda_e x + \mu_e y)\, dS_e \ldots \quad (16),$$

where λ, μ, ν are the direction cosines of the normal drawn *from* the solid, and the suffix denotes the surface.

Taking the origin in one end of the prism, and supposing its length l, we have $z = 0$ over the one flat end and $z = l$ over the other; thus S denoting the area of one end,

$$\iint PzdS = PlS = Pv,$$

where v is the volume of the *material.*

Over the two prismatic surfaces

$$\lambda_i x + \mu_i y = -\varpi_i, \quad \text{and} \quad \lambda_e x + \mu_e y = \varpi_e,$$

where ϖ_i and ϖ_e represent the perpendiculars from some internal fixed point on the tangent planes to the two surfaces. But obviously

$$\iint \varpi_i dS_i = 2v_i, \qquad \iint \varpi_e dS_e = 2v_e,$$

where v_i and v_e are the volumes included within S_i and S_e respectively. Thus (16) gives at once

$$Ev\bar{g} = Pv + 2\eta\,(p_e v_e - p_i v_i).$$

Clearly $\bar{g} = \delta\bar{l}/l$, where $\delta\bar{l}$ represents the mean change in length of all the longitudinal "fibres" of which the prism is composed. Thus

$$\delta\bar{l}/l = \frac{P}{E} + \frac{2\eta}{E}\left(\frac{p_e v_e - p_i v_i}{v}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (17).$$

As in the isotropic circular cylinder, there are three principal cases:

$$\text{(i)} \quad p_e = 0, \quad Pv = p_i v_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (18),$$

$$\delta\bar{l}/l = p_i(v_i/v)/3k_3 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (19);$$

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* 'Camb. Phil. Soc. Trans.,' vol. 15, Eqn. (15), p. 317.

$$\text{(ii)}\quad p_i = 0, \quad \mathrm{P}v = -p_e v_e \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (20),$$

$$\delta l/l = -p_e(v_e/v)/3k_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (21);$$

$$\text{(iii)}\quad p_i = p_e = -\mathrm{P} = p \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (22),$$

$$\delta l/l = -p/3k_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (23).$$

Here

$$k_3 \equiv \tfrac{1}{3}\mathrm{E}/(1-2\eta) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (24).$$

Noticing that $\dfrac{v_i}{v} = \dfrac{\text{Cross-section within } \mathrm{S}_i}{\text{Section of prism wall}}$,

and similarly for v_e, it is obvious that Cases (i) and (ii) answer respectively to uniform internal and external pressures in a hollow prism whose ends are covered by caps.

The above results are true—under the same limitations as for the isotropic cylinder—whatever be the shapes of the prismatic sections, and irrespective of whether they be similar to one another or not. If, however, the prismatic walls be thick, or the contours of the cross sections be irregular and dissimilar, there *may* be, so far as the above proof is concerned, considerable differences between the longitudinal alteration of different "fibres," and to obtain a satisfactory observational value for δl might be troublesome.

In the case of a right circular cylinder whose two surfaces are co-axial there cannot, of course, be any buckling, and if the walls are thin, δl will be given satisfactorily by measurement of a single generator.

The elastic modulus k_3 defined by (24) represents (*mean* surface pressure ÷ reduction in volume), in a unit cube when only the faces perpendicular to z are under pressure, the remaining four faces being unstressed. It is distinct from the true bulk modulus k, answering to uniform pressure the same in all directions, which is given by

$$\frac{1}{k} = \frac{1-2\eta}{\mathrm{E}} + 2\left(\frac{1}{\mathrm{E}'} - \frac{\eta}{\mathrm{E}} - \frac{\eta'}{\mathrm{E}'}\right) \ldots\ldots\ldots\ldots\ldots\ldots \quad (25),$$

or

$$\frac{1}{k} = \frac{1}{k_3} + 2\left(\frac{1-\eta'}{\mathrm{E}'} - \frac{1-\eta}{\mathrm{E}}\right) \ldots\ldots\ldots\ldots\ldots\ldots \quad (26).$$

"On the Colouration of Glass by Natural Solar and other Radiations." By Sir WILLIAM CROOKES, D.Sc., F.R.S. Received January 17,—Read January 26, 1905.

It is well known that many samples of colourless glass containing manganese slowly assume a violet tint when exposed to sunlight. This effect is frequently seen in plate-glass windows having a southern aspect; watched from year to year they assume a more and more pronounced amethystine hue. The introduction of manganese into glass is to neutralise the colour caused by the presence of iron. Iron gives the glass a greenish tint, and the addition of manganese binoxide performs the double object of oxidising the green proto-salt of iron to the per-salt, and also of imparting a purple shade which neutralises the green-yellow tint of the silicate of peroxide of iron.

In 1903, I received from two separate correspondents specimens of glass coloured an intense purple. I quote the following sentences from the covering letters:—

Mr. A. Ernest Williams writes:—

"While residing at Uyuni, in Bolivia, last year, at an altitude of nearly 4000 metres, my attention was called to the fact that all transparent white glass when thrown out on the 'Pampa' in a short time assumes a violet hue, which becomes more marked with time. I was told that all specimens were thus affected, and that when taken to sea level at Antofagasta they lost their colour. This latter statement I hardly believe, as I have had some pieces with me now on low level for nearly a year, and they have not lost the colour.

"I now notice that all transparent white glass thrown on rubbish heaps, even at low level, assumes this violet colour, though only to a slight degree, and I am curious to know the cause, being more interested since reading that radium so affects glass.

"I may mention that Uyuni is situated on the great central plain of Bolivia, which plain has evidently formed the bed of an inland sea or lake, for I have found quantities of minute shells there. Not far off to the south and south-west are borax fields, and still further west, nitrate. To the north-east are the mountains of Pulacayo and Cuzco (not the great Cuzco), and electrical disturbances are of almost daily occurrence. I can fully confirm Sir Martin Conway's description of the battles between the mountains, where lateral discharges are plainly visible. I am sending you by post a small specimen of the glass."

About the same time I received some specimens of purple-coloured glass from Mr. Thomas Wilson, from Iquique, Chile. In a subsequent letter answering some enquiries, he sent a further quantity of the coloured glass, saying:—

"You will notice a great variety in the depth or degree of tint in the different pieces, which may be attributable to the varied length of the exposure of each to the action of the sun's rays. It seems to me that some of the pieces have lost somewhat of their depth of colour since I picked them up, but this may be an impression only. The two pieces forming together the bottom of a broken tumbler, and which have a deeper tint than any of the rest, were found about twenty paces apart in an old Oficina that had been uninhabited for 27 years. It is impossible to give any idea of the length of exposure of the remaining pieces to the sun's rays, as I have obtained them from all parts of the Pampa over an extent of nearly 100 miles. The samples I send you were originally white glass, and although an abundance of glass of various colours is to be found, yet I send you none, as it would not be easy to say what the original colours had been previous to exposure."

The pieces of glass referred to above are of all depths of tint, from deep violet, almost black in thick pieces, to pale amethyst. Analysis shows the glass to contain manganese. Heating the glass in a covered crucible to its softening point, discharges the colour, leaving the glass white and transparent.

The colouration is not superficial. On immersing a piece of the coloured glass in a liquid of about the same refractive index as itself, the colour is seen to have penetrated throughout the mass.

At first sight the explanation of this phenomenon would seem to be that it is produced by the action of light, the intense radiation occasioning a re-arrangement of the oxygen molecules in the glass, the ferric salt becoming ferrous, and the manganous salt changing to a manganic compound.* The change of colour might then be expected to be noticed in any part of the world where broken glass is thrown about and the sun's rays are very intense. In the Transvaal, where both these conditions are well fulfilled, I have neither heard of nor noticed any such colouration, and it would be interesting to hear if travellers in other tropical countries have observed any such change of colour of glass.

Probably height above sea level has much to do with the phenomenon. At a height of 4000 metres nearly half the atmosphere is beneath one's feet, and that which remains will allow rays of shorter wave-length to pass through than the atmosphere at sea level will transmit.

For this reason it is not necessary to invoke another mode of explanation that might possibly suggest itself. It now has been well established that many natural bodies, water from great depths, some samples of earth and rock, air from underground sources, together with some minerals, are more or less radio-active. Radium, acting for a few days, even through quartz, will produce as intense a colouration in a piece of this glass as exposure to the sun on the Pampa has taken years to effect. It is hardly conceivable that there can be a special radio-activity of the soil in certain parts of Chile and Bolivia sufficiently powerful to produce the effect.

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* In this connection it may be of interest to recall the fact that in the early days of photographic research the ultra-violet rays of the spectrum were called the "deoxidising rays."

A piece of the coloured glass, bleached by heat, was put close to a quartz tube in which about 15 milligrammes of pure radium bromide was sealed up. In the course of a few hours a faint amethystine tint could be distinguished on the glass, and in a week the tint was equal to the deep colour of the unbleached specimen. A duplicate piece of the same glass which had been bleached by heat, kept away from radium, remained colourless for seven weeks.

A piece of the deepest purple-coloured glass was put on a sensitive photographic film, and kept in the dark in contact with it for 34 days. No trace of action could be detected on developing.

The purple glass which had been bleached by heat and then coloured purple again by radium, was put in close contact with a sensitive film for 24 hours. On developing, no trace of action could be seen.

The darkening effect produced by radium on bodies exposed to its emanations is very general. Quartz, mica, glass of all kinds, and the diamond may be specially mentioned. In a paper recently read before the Royal Society "On the Action of Radium Emanations on Diamond,"* I showed that the β-rays (electrons) and γ-rays not only effected a superficial darkening, converting the surface of the diamond into graphite, but the body colour of the stone was changed from pale yellowish-brown to bluish-green; and I suggested the explanation that the action might be chemical, the ferric state of the iron being reduced to the ferrous state, and the colour thereby changing from yellow to blue-green.

In the year 1855, I tried a series of experiments with a spectrum camera furnished with two quartz prisms and a quartz lens, with the object of ascertaining if the atmosphere exerted any absorptive action on the more refrangible rays of light. Photographs of the solar spectrum were found to reveal lines of higher and higher refrangibility the nearer they were taken to mid-day, and arguing from this I concluded that the "noon-day spectrum at midsummer ought to contain more and higher rays than are possessed by the corresponding spectra at any other time of the year." The examination of the photographed spectra was continued through the summer, photographs being taken at noon whenever the sun was clear, and I found that "as the light came less obliquely through the atmosphere, new rays began to be apparent, until at midsummer, when the sun was on the meridian, I succeeded in obtaining evidence of the existence of rays which the most prolonged exposure failed to detect at any other time."

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* 'Roy. Soc. Proc.,' June, 1904, vol. 74, p. 47.

I may perhaps be pardoned for quoting from my paper on the subject the following passage, written 50 years ago.*

"Some curious speculations arise from these facts. Should we be able, by working under a vertical sun, and with every advantage of cloudless sky, etc., to increase still more the length of our spectrum? Can we attain the limit of solar refrangible rays in this direction? Or is it not more likely that there are emanating from the sun torrents of rays which never approach the earth—rays which, beating against the upper stratum of the atmosphere, are themselves destroyed, but whose vibrative energy is transmitted to us with increased wave-length and lowered refrangibility, in the form of heat or light?"

Sunlight and radium both produce similar effects in these respects. Their modes of action are known to be in the main very different; but it has been clearly shown that, in general, variation of time being disregarded, what radium is capable of doing in the way of inducing chemical change, ionising gases, producing phosphorescence, and impressing a photographic plate, sunlight will also effect.

[*March* 6.—I am indebted to Professor McLeod for the following historical note on the action of light on glass:—"T. Gaffield, of Boston, U.S., 'B.A. Report,' 1872, Sect., pp. 37—38. Bontemps, 'C.R.' 69, 1869, 1075—1078; 'Cosmos,' 6, 1870, 66—75. In the 'C.R., Bontemps presented to the Academy the results obtained by Gaffield, together with some of his own. He refers to the experiments of Faraday, which are described in 'Quart Jl. Sci.,' 19, 1825, 341. Faraday describes the change to violet which took place in certain glass after nine months' exposure to sunlight in London, and mentions the colour of the window glass in houses in Blackfriars Bridge Road, now pulled down, but which I well remember. Bontemps also mentions work by Pelouze in 1867, described in 'C.R.' 64, pp. 53—66, in which he attributes the yellow colour, produced in some glass, to the formation of sulphides from the sodium sulphate by the action of ferrous oxide, an explanation which Bontemps thinks improbable."

Professor Judd called attention, when the paper was read, to the deep colouration of the glass in the old greenhouses at Kew, in the parts where it has been exposed to light. Glass coloured green with oxide of iron for use in the forcing houses (as proposed by the late Robert Hunt) is found by long exposure to sunlight to gradually lose this colour and to become perfectly colourless. Subsequently a purple colour, due to small admixture of manganese in the original frit, makes its appearance. Visitors to the various houses in Kew Gardens can easily verify these facts for themselves, as the most varied tints, from green to colourless and purple, may be seen in different panes of glass, according to the period at which they have been put in during repairs.

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* 'Journal of the Photographic Society of London,' vol. 2, p. 293.

Professor Judd has enabled me to try the action of radium emanations on specimens of this glass. Fifteen milligrammes of pure radium bromide sealed in a quartz tube were put close to a sample of the deepest green glass. In two days appreciable darkening took place, and in 10 days the darkening was very marked.

A similar experiment was tried on a sample of the purple-tinted glass; here also the action was the same as in the former case, and in 10 days the darkening was about the same. Allowing for the apparent alteration of colour caused by the initial tint of the two pieces of glass, I should say the colour produced by radium was similar in each case, and was of the same purple colour as that caused by long exposure to sunlight.]

"On the Comparison of the Platinum Scale of Temperature with the Normal Scale at Temperatures between 444° and −190° C., with Notes on Constant Temperatures below the Melting-point of Ice."

By Morris W. Travers, D.Sc., F.R.S., and A. G. C. Gwyer, B.Sc. Received January 11,—Read January 26, 1905.

Introduction.—During the last few years one of us has been engaged in researches involving the accurate measurement of low temperatures. The measurements were made by means of gas thermometers, of the constant volume type, filled with hydrogen, or with helium, at an initial pressure of 1000 mm. As, however, this method proved cumbrous and inconvenient, it was decided to standardise a platinum resistance thermometer of the Callendar type against the gas thermometer, and to employ it in future investigations. The comparison of the thermometers between −190° and 444° C. has been carried out with considerable accuracy, and as the range of temperature overlaps that investigated by Callendar and Griffiths, and by Harker and Chappuis, we have decided to publish our results, though from our own standpoint the work is only considered as preliminary to other investigations.

In expressing our results we have employed Callendar's notation. Thus, when R_0 is the resistance of a coil of platinum wire at the melting point of ice, and R_{100} is its resistance at the temperature of saturated steam under absolute standard pressure, which in the laboratory of University College, Bristol, is equivalent to 759·55 mm. of mercury at zero, the value of the coefficient of change of resistance, α, is given by

$$\frac{R_{100} - R_0}{100R_0} = \alpha.$$

If the coil has a resistance R at the platinum temperature T_p,

$$R = R_0 (1 + \alpha' T'_p).$$

Callendar and Griffiths[*] have shown that between 0° and 444·55°, the boiling point of sulphur on the constant pressure nitrogen scale, the difference, Δ, between the platinum and the gas scales can be calculated by means of a parabolic formula,

$$\Delta = \partial \left(\frac{T}{100} - 1 \right) \frac{T}{100};$$

where T is the temperature (Centigrade), on the gas scale, and ∂ is a constant. Callendar has suggested that this principle should form the basis of a practical scale of temperature, and Messrs. Johnson and Matthey have taken much trouble to prepare pure platinum for the purpose. For this material α is about 0·00388 or 0·00390, and the value of ∂ about 1·5.

Previous Investigations.—Harker and Chappuis[†] have compared a set of platinum thermometers, for which the value of α was about 0·003865, with the constant volume nitrogen thermometer, and have found that the difference between the two scales of temperature can be calculated by means of Callendar's formula, taking for ∂ values between 1·54 and 1·55. The comparison was carried out over a range of temperature between −23° C. and 455° C., and the errors at the higher temperatures did not exceed 0·2°.

More recently, Harker[‡] has extended this investigation, comparing the platinum thermometers with a *constant volume* nitrogen thermometer standardised at 0°, 100°, and 444·55°, the latter being Callendar's value for the boiling point of sulphur on the *constant pressure* air scale. The observations, therefore, really refer to the constant pressure air scale. In this research he employed a resistance thermometer described in the British Association Report for 1899 (p. 243), for which the value of α is 0·00389. Taking 1·51 for the value of ∂, he found that the temperatures calculated from observations of the two thermometers showed a maximum difference which only exceeded the probable error of measurement over the higher part of the range.

At the end of his paper Harker gives a table of the corresponding values of T_p and Δ, calculated on the basis $\partial = 1·50$, between −200° and 1,100°. As it is well-known that the formula cannot be applied to the calculation of the difference between the two scales at low temperatures, this appears to be unnecessary and misleading.

Several independent investigators have compared platinum and gas thermometers at low temperatures, but for the reason that they did not employ standard platinum, or did not succeed in maintaining sufficiently steady temperatures, the results are not strictly comparable with those already referred to. The results of Dewar and Fleming, and of Olszewski have been summarised by Callendar;[*] they show varying divergences from the parabolic formula, depending on the kind of platinum employed. Holborn and Wien[†] compared the platinum, air, and hydrogen scales at temperatures between 300° and 500°, and again at − 78° and at − 190°. They employed a platinum coil enclosed within the gas thermometer bulb, so as to minimise the error due to varying temperature. They found with platinum for which α was equal to 0·00378 the parabolic formula gave a very close approximation between − 78° and 500°, but showed a deviation of 2·3° at − 190°. We find that the deviation becomes marked even at − 78°.

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[*] 'Phil. Trans.,' A, 1891, p. 119.

[†] 'Phil. Trans.,' A, 1900, vol. 194, p. 37.

[‡] 'Phil. Trans.,' A, 1904, vol. 203, p. 343.

Apparatus Employed.—The thermometer consisted of a coil of platinum wire about 130 cm. long, having a resistance of 7 ohms at the ice point. The ends of this wire were fused to leads about 0·3 mm. in diameter, and these leads and the ends of the compensating leads were soldered respectively to the ends of four insulated copper wires, enclosed in a lead tube. The resistance was measured by means of resistances constructed by the Cambridge Scientific Instrument Co., to the design of Professor Callendar. The individual resistance coils were carefully calibrated by one of us before the experiments were commenced. As the coils were of platinum-silver alloy, for which the temperature coefficient is 0·00024, it was necessary to observe their temperature each time an observation was made, and to reduce the result to zero. The resistance plugs were cleaned before each experiment, and the zero point on the sliding resistance, which rarely varied by more than 0·0001 ohm between individual sets of experiments, or by more than 0·0005 ohm in the course of two years, was always observed. A home-made galvanometer of the two-coil astatic type was employed, and with the highest resistance in the circuit it was possible to adjust the slider with an accuracy corresponding to 0·0002 ohm. In connection with these instruments the usual arrangement of keys, etc., was employed.

The Fundamental Interval of the Thermometer.—In determining the ice and steam point the platinum coil and leads were enclosed in a glass tube containing some paraffin to the height of about 3 cm. above the coil. An identical result for the ice point was obtained by protecting the thermometer by means of a glass tube with holes in the side of it and immersing it directly in melting ice and water. The following are the results of the experiments, which need not be given in detail:—

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[*] 'Phil. Mag.,' February, 1899.

[†] 'Wied. Ann.,' 1896, 59, p. 213; 1901, 6, p. 242.

Date and place.	Ice point measured.	Steam point measured.	a.
July, 1903, London	Three times	Twice	0·0038989
October, 1903, London ...	,,	Once	0·0038977
July, 1904, Bristol	,,	Twice	0·0038988

The probable value of the coefficient is, therefore, about 0·003899. It may be pointed out that the maximum variation in the ice point would correspond to one unit in the next place of decimals. The variations in the experimental values of a are entirely attributable to errors in the determination of the steam point. In any case an error of one unit in the last place of decimals is insignificant and amounts only to an error of :—

$$0{\cdot}005^{\circ} \text{ at } +33^{\circ}\ T_p$$
$$0{\cdot}05 \quad ,, \quad -200^{\circ}\ T_p$$

Comparison of the Platinum and Hydrogen Thermometers in Liquid Air.—The hydrogen thermometer, employed for this purpose, has already been described by one of us in conjunction with Drs. Senter and Jaquerod.* The method of working with and the degree of accuracy of the readings have been discussed in detail, and it is only necessary to state that the maximum errors never exceed 0·05° at −190° C. At the ice point the pressure of the gas in the thermometer was about 1000 mm.

The platinum thermometer was held in a clamp so that the coil was almost in contact with the bulb of the platinum thermometer. The liquid air surrounding them was contained in a cylindrical silvered vacuum-vessel 20 cm. in diameter and 5 cm. deep, which, in the second and third set of experiments, was placed inside a somewhat larger silvered vacuum-vessel. Some liquid air was poured into the space between the two vessels, and both the opening of the annular space and the mouth of the inner vessel were plugged with sheep's wool.

With this arrangement the rate of rise of temperature as the air evaporated amounted to 0·002° per minute. And under these conditions it can safely be assumed that the temperature of neither thermometers differed from that of the bath by an appreciable amount.

It is noteworthy that under such conditions liquid air appears to evaporate from the surface and does not undergo regular fractionation.

The following are the results of our experiments :—

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* 'Phil. Trans.,' A, vol. 200, 1902–3.

A. $R_0 = 7{\cdot}3322$ ohms. $\alpha = 0{\cdot}003899$.

Date.	R.	T_p.	T.H. scale.	Δ(obs.).	Δ(∂ = 1·90).
June 11, 1908	1·5141	−203·53	−192·72	10·84	10·72
June 20, „	1·6170	−199·91	−189·45	10·36	10·42
June 23, „	1·5265	−203·13	−192·27	10·86	10·68
June 24, „	1·5459	−202·45	−191·71	10·74	10·65
„ „	1·5799	−201·26	−190·62	10·64	10·60
June 25, „	1·6257	−199·66	−189·18	10·48	10·39
„ „	1·6289	−199·54	−189·08	10·51	10·38
„ „	1·5215	−203·31	−192·48	10·83	10·72

In this set of experiments the liquid air was contained in a single silvered vacuum vessel.

B. $R_0 = 7{\cdot}3319$ ohms. $\alpha = 0{\cdot}003899$.

Date and time.	R.	T_p.	T.H. scale.	Δ.	Δ(∂ = 1·90).
Nov. 3, 1908, 12.00 A.M.	1·5901	−200·86	−190·33	10·53	10·50
„ „ 12.15 P.M.	1·5909	−200·82	−190·29	10·53	10·49
„ „ 2.00 „	1·6072	−200·25	−189·78	10·47	10·45
„ „ 5.00 „	1·6123	−200·07	−189·61	10·46	10·43
Nov. 4, „ 11.00 A.M.	Vacuum vessel refilled with liquid air.				
„ „ 12.15 P.M.	1·6578	−198·50	−188·14	10·37	10·30
„ „ 2.15 „	1·6754	−197·86	−187·61	10·25	10·25
„ „ 3.00 „	1·6781	−197·77	−187·57	10·20	10·24

C. $R_0 = 733{\cdot}19$. $\alpha = 0{\cdot}003899$.

Date and time.	R.	T_p.	T.H. scale.	Δ.	Δ(∂ = 1·90).
Nov. 11, 1908, 2.00 P.M.	1·6364	−199·24	−188·84	10·40	10·36
„ „ 3.00 „	1·6487	−198·80	−188·51	10·29	10·33
„ „ 3.55 „	1·6583	−198·46	−188·14	10·32	10·30
„ „ 4.50 „	1·6668	−198·16	−187·85	10·31	10·27

The second and third sets of experiments, in which the rate of rise of temperature was exceedingly slow, are probably the most accurate.

If we calculate the value of Δ for the Centigrade temperature −190 for value of ∂ corresponding to 1·90 and 1·50, we find

Δ (T = 190, ∂ = 1·90) .... 10·47°
Δ (T = 190, ∂ = 1·50) .... 8·27°

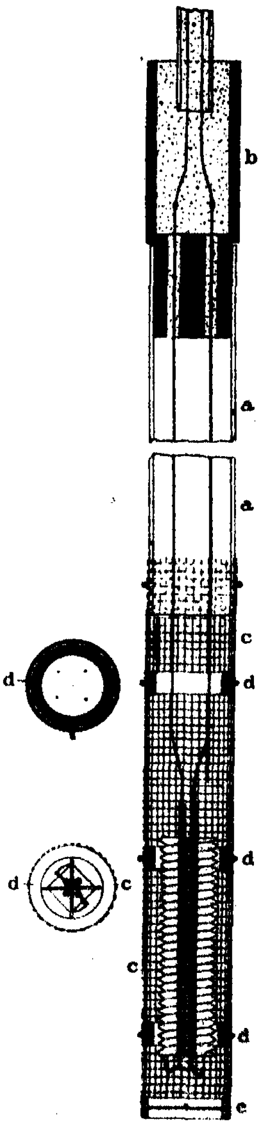
This difference is of the same order as that found by other investigators.

Comparison of the Thermometers at the Temperature of Solid Carbonic Acid and Alcohol.—A mixture of solid carbonic acid and ether or rectified methylated spirit has frequently been employed as a means of maintaining a constant temperature. Olszewski states that the temperature remains constant so long as the mixture has the consistency of butter, but that as soon as ether appears on the surface, the temperature begins to rise. He gives the temperature as −78·2° C.

Our experiments lead to the conclusion that to obtain the best results the solid carbonic acid should be free from lumps, and should be added to the spirit—for there is no advantage in using ether—till the mixture has the consistency of a fairly thin paste, and can be stirred with a glass rod. The stirring should be repeated at short intervals.

At the outset of the experiments we were met with the difficulty of exposing the platinum coil to the action of the mixture, and at the same time protecting it from strain during the process of stirring. When the bare wire was exposed to the mixture, it was found that the values of R_0 before and after an experiment were in every case different, and when the coil was enclosed in a glass tube with holes in the side of it, the circulation of the mixture was obstructed, and the results were discordant. The difficulty was at last overcome by surrounding the coil with a tube of wire gauze, as is shown in fig. 1. The glass and gauze tubes are shown in section, the thermometer in plan.

FIG. 1.



a, Glass tube passing inside gauze tube and connected to vulcanite head *b* of thermometer. *c*, Nickel gauze tube made rigid by binding it with wire on to the glass tube *a*, and on to thin vulcanite rings *d d*, which also serve to prevent the coil and leads from touching the gauze. *e*, Brass ring and wire grating soldered to tube.

The gas thermometer was the same as was used in the liquid air experiments. As, however, the volume of the bulb was known only at 100°, 0°, and − 185° C.,* the volume at − 80 was calculated by means of a parabolic formula with two constants. We have taken as our values for the volume—

100°	………	24·332 c.c.
0°	………	24·262 „
− 78°	………	24·216 „
− 185°	………	24·162 „

The arrangement of the thermometers and the vacuum-vessels was the same as in the liquid air experiments, the only difference in the manner of carrying out being that the bath was stirred at intervals. The following are the results :—

A. $R_0 = 7 \cdot 3319$ ohms. $\alpha = 0 \cdot 003899$.

Date and time.	R.	T_p.	T.H. scale.	Δ.	$\partial T/\partial$ time.
Oct. 22, 1903, 3.55 P.M.	5·0213	−80·83	−78·25	2·58	
„ „ 4.25 „	5·0230	−80·77	−78·21	2·57	0·002
„ „ 5.00 „	5·0242	−80·74	−78·19	2·55	0·001
Oct. 23, „ 10.00 A.M.	5·0276	−80·62	—	—	0·000
„ „ 5.30 P.M.	5·0448	−80·02	−77·23	2·79	0·001
Oct. 24, „ 10.00 A.M.	5·4336	−66·41	−64·40	2·01	0·004
„ „ 10.20 „	5·4506	−65·82	−63·72	2·10	0·103
„ „ 2.30 P.M.	5·6961	−57·23	−55·47	1·76	0·035
„ „ 3.25 „	5·9782	−47·35	−46·04	1·31	
„ „ 4.15 „	6·0160	−46·06	—	—	

B. $R_0 = 7 \cdot 3319$ ohms. $\alpha = 0 \cdot 003899$.

Date and time.	R.	T_p.	T.H. scale.	Δ.	$\partial T/\partial$ time.
Oct. 27, 1903, 12.20 P.M.	5·0194	−80·87	−78·28	2·59	
„ „ 2.20 „	5·0223	−80·80	−78·27	2·53	0·006
„ „ 4.15 „	5·0243	−80·73	−78·18	2·55	0·006
Oct. 28, „ 10.00 „	5·0441	−80·04	−78·38	2·66	
„ „ 4.00 „	5·0545	−79·68	−77·09	2·59	

Though these results point to the conclusion that a mixture of solid carbonic acid and alcohol varies in temperature by less than one degree over a period of more than 36 hours, it is only during the first few hours that it remains steady enough for this purpose. Taking the first three observations of each set we obtain the result—

Mean T_p.	Mean T.H. scale.	Δ.	∂ (calc.).
− 80·79°	− 78·23	2·56	1·84

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* 'Phil. Trans.,' A, vol. 200, p. 138.

Taking the value for ∂, viz., 1·90, obtained by comparing the thermometers in liquid air, we obtain for Δ the value 2·64, introducing an error of less than 0·1°.

Attempts to Maintain Constant Temperatures below the Freezing Point of Water.—We have not succeeded in making comparisons of our thermometers at temperatures other than − 78 and the temperature of liquid air. The use of liquefied gases such as nitrous oxide and ethylene in quantities up to 100 c.c. did not give sufficiently constant temperatures, and larger quantities could not be procured except at a prohibitive cost. Attempts were also made to compare the thermometers in baths of melting solids, such as ethyl acetate, but without success.

Comparison of the Thermometers at the Transition Point of Sodium Sulphate.—Richards and Wells* have shown that the transition point of sodium sulphate decahydrate to the anhydrous salt may be considered as a standard temperature in thermometry. They measured this temperature on three Baudin thermometers and on one Tonnelot thermometer, and found, as the mean of results which differed among themselves by 0·01°, the value 32·383 on the normal scale.

For the purpose of measuring the transition temperature on the platinum scale, we prepared some pure sodium sulphate, dried the crystals, and ground them to powder. The powder was heated in a beaker in a water-bath at about 40° C. till the mass became pasty, and was then transferred to the vessel surrounding the thermometer, which was enclosed in a tube containing paraffin oil (p. 532). The vessel containing the sulphate was a glass cylinder, 8 cm. wide and 20 cm. deep, with a round bottom. The cylinder was supported in a large thermostat, and it was found that when the temperature of the latter was kept at 32°·6 C. the temperature of the sodium sulphate remained quite steady, and was not affected by stirring.

Date.	R_0.	R.	T_p.	T_n.	Δ.
Oct. 12, 1904	7·3325	8·2704	32·799	32·383	−0·416
Oct. 18, „	„	8·2701	32·788	„	−0·405
Oct. 26, „	„	8·2706	32·805	„	−0·422

The value of ∂ corresponding to the mean value of Δ is 1·98, and it will be observed that this is identical with that obtained at − 190°, and very close to the value at − 78° C., viz., 1·84. Indeed, it appears that a parabolic formula may be applied to the calculation of Δ between 30° and − 190° C. with a maximum error, probably not greater than 0·2° C. at about − 100° C. This result is mainly dependent on the accuracy of our determination of the transition point of sodium sulphate on the platinum scale and that of Richards and Wells on the hydrogen scale. If this result is correct it would appear that since the value 1·5 for ∂ gives for Δ 0·329 at 32·38° C., there must be at this temperature a difference of 0·08° between the constant pressure air scale and the constant volume hydrogen scale.

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* 'Zeit. Phys. Chemie,' 1898, vol. 26, p. 690; 1903, vol. 43, p. 465.

Comparison of the Thermometers at Higher Temperatures.—In order to make certain that our thermometer behaved normally at higher temperatures, we repeated the original experiments of Callendar and Griffiths, and obtained the same result.

The Boiling Point of Naphthalene, Benzophenone and Sulphur on the Platinum Thermometers.—The apparatus employed in these experiments was exactly similar to that described by Callendar and Griffiths.* In the case of the two organic substances the top of the glass Meyer tube was closed by a cork, and a bent glass delivery tube served to condense the vapour and conduct the liquid into a receiver. The constancy of the temperature while the substance distilled served as an indication of its purity.

The naphthalene was first crystallised from absolute alcohol, was then distilled, and subsequently redistilled before each experiment. The benzophenone (Kahlbaum) was dissolved in alcohol, water was added to the hot solution till it appeared cloudy, and then ether was added till it again became clear. On standing large crystals separated, and these were taken, dried in a desiccator, and distilled.

In the sulphur experiments we sometimes employed pure sulphur, sometimes crude roll sulphur, without observing any difference in the result.

Naphthalene.—Callendar and Griffiths† taking 444·55 for the boiling point of sulphur on the constant pressure air thermometer, measured the boiling point by means of a platinum thermometer, and found the value 217·94. Crafts‡ measured the boiling point by means of an air thermometer and found 218·06. Recently Jaquerod and Wassmer§ have determined the vapour pressure on the scale of a constant volume thermometer, filled with hydrogen at a pressure of 500 mm. at the ice point. Their results for the temperatures corresponding to pressure in the neighbourhood of 760 mm. may be expressed in the form

$$T_p = 217{\cdot}68^\circ + 0{\cdot}057\,(p - 760).$$

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* 'Phil. Trans.,' A, 1891, p. 119.

† *Loc. cit.*

‡ 'Bulletin Soc. Chim.' [2], vol. 39, p. 282.

§ 'J. de Chim. Phys.,' vol. 2, p. 52.

Results ($\alpha = 0{\cdot}003899$).

Date.	R_0.	R.	T_p.	$T_p + \Delta(\partial - 1{\cdot}5)$.	T (J. and W.).
Nov. 7, 1904..	7·2325	13·4291	213·20	216·99	216·63
Nov. 11, „ ..	7·3322	13·4490	212·91	217·64	217·28
„ „ ..	7·3322	13·4487	212·90	217·63	217·28

It will appear that our results, calculated on this basis, are 0·36 higher than those of Jaquerod and Wassmer, and 0·10 higher than those of Callendar and Griffiths. The agreement with the latter is, however, good enough to prove our point.

Benzophenone.—Callendar and Griffiths* found the boiling point to be 305·8, while Jaquerod and Wassmer's result can be expressed in the form

$$T_p = 305{\cdot}44 + 0{\cdot}062\,(p - 760).$$

The result of the single experiment which we carried out is as follows—

Date.	R_0.	R.	T_p.	$T_p + \Delta(\partial = 1{\cdot}5)$.	T. (J. and W.).
Nov. 18, 1904	7·3322	15·8171	296·73	306·19	305·83

The result calculated in this manner is again 0·36° higher than that of Jaquerod and Wassmer, and consequently agrees exactly with that of Callendar and Griffiths.

Sulphur.—According to Callendar and Griffiths the boiling point of sulphur on the constant pressure air thermometer is given by the expression

$$T_p = 444{\cdot}53 + 0{\cdot}082\,(p - 760).$$

Chappuis and Harker† find for the boiling point of nitrogen on the constant volume nitrogen scale the value 445·27°.

Results ($R_0 = 7{\cdot}3325$, $\alpha = 0{\cdot}003899$).

Date.	R.	T_p.	T (C. and G.).	Δ.	∂.
Sept. 28......	19·3738	421·08°	444·37°	23·29°	1·52
Sept. 29......	19·3817	421·36	444·24	22·81	1·50
Oct. 4......	19·3806	421·32	444·06	22·74	1·49
„	19·3766	421·18	„	22·88	1·50
„	19·3735	421·08	„	22·98	1·50
„	19·3825	421·39	„	22·67	1·48

As the mean of these results we may take—

T_p.	T (C. and G.).	∂.
421·23°	444·14	1·50

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* *Loc. cit.*

† 'Brit. Assoc.,' 1899, p. 245.

or taking Chappuis and Harker's value for the boiling point, which is 0·74° higher, we obtain for ∂ 1·54.

Conclusion.—As might be expected, it is possible to apply the parabolic formula of Callendar and Griffiths to the recalculation of the differences between the platinum scale of temperature and the scale of the gas thermometer, though the range through which it is applicable, and the value of the constant ∂, precludes the possibility of employing it except for interpolation. A standard scale of temperature, based on Callendar's three fixed points, using standard wire, and taking 1·5 for the value of ∂, would obviously lead to absurd results at low temperatures; and the converse may be said of our own observations. To sum the matter up, we will tabulate the results that have been referred to in this paper.

Nature of gas thermometer.	Observer.	∂.
Constant pressure air (0° to 444°)	Callendar and Griffiths	1·50
Constant volume nitrogen (−23° to 445°)	Chappuis and Harker	1·54
Constant volume nitrogen standardised by constant pressure air at 444° (500° to 1000°)	Harker	1·51—1·49
Constant volume hydrogen (−190° to 34°)	Travers and Gwyer	1·90

"The Arc Spectrum of Scandium and its Relation to Celestial Spectra."

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Very little has been published regarding the spectrum of this rare element. The records of Thalen,* and Exner and Haschek,† are the only ones previously given, the former observer confining his attention to the spark spectrum, whereas Exner and Haschek have recorded the lines under both arc and spark conditions. In the latter lists, however, no lines are given in the region less refrangible than λ 4744·0. Rowland, in his "Tables of Solar Wave-lengths," certainly ascribes a small number of solar lines to scandium, but, of course, no indication is there given as to the relation of these lines to others which occur in the scandium spectrum, either in regard to number or intensity. In connection with the work at Kensington on stellar and other celestial spectra, it has been found that in some types of spectra scandium is conspicuously represented by some of its lines, in fact, amongst the rarer elements it apparently stands by itself from this point of view. This prominence of scandium lines in some stellar spectra, and particularly in the chromospheric spectrum, makes it desirable to give as complete a record of the lines as possible, and also to analyse them in relation to their appearance or non-appearance in extra-terrestrial spectra.

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* 'Öfversigt af Kongl. Vetensk. Akad. Forhandl.,' vol. 38, No. 6, p. 13.

† 'Wellenlängen-Tabellen für Spektralanalytische Untersuchungen auf Grund der Ultravioletten Funkenspektren und Bogenspektren der Elemente,' Leipzig und Wien, Franz-Deuticke, 1902.

Some time ago Sir William Crookes was good enough to send a sample of scandium oxalate, and very good photographs of the arc spectrum have been obtained with a larger Rowland concave grating, having a ruled surface of 5¾ × 2 inches (14½ × 5 cm.), and a radius of 21 feet 6 inches. The scale of the photographs is such that the distance between K and D is 30¼ inches, or 77 cm. This is equivalent to 2·6 tenth-metres per millimetre. The scandium oxalate was admittedly impure, and for the purpose of eliminating lines due to impurities, the spectrum has been directly compared with the spectra of all the chemical elements available at Kensington, which were photographed under identical instrumental conditions. The chief sources of impurity were found to be cerium, thorium and ytterbium. The lines of the first two elements were easily eliminated by comparison with the Kensington photographs of their respective arc spectra. In the case of ytterbium it was a more difficult matter, as this is one of the elements not investigated at Kensington. The elimination of its lines has, however, been accomplished as far as possible, by ascertaining whether there were lines in the scandium photograph in the position of the stronger lines of ytterbium as recorded by Thalen,* and Exner and Haschek.† If such were found to be the case, and the intensity in the scandium photographs such that the line was thought to be due to ytterbium, it was discarded from the list of scandium lines.

The fiducial lines used for the reduction of wave-lengths were the H and K lines of calcium (which occur as impurity lines in the scandium spectrum), and Rowland's solar-scandium lines 3907·62, 4020·55, 4082·59, 4247·00, 4314·25, 4400·56, 4670·59, 5672·05. The coincidence of these lines was first confirmed by a direct comparison of the Kensington photographs of the solar and scandium spectra. In addition to the foregoing, well-marked scandium lines were found to be exactly coincident with the isolated solar lines 5031·20, 5239·99, and 5527·03, for which Rowland had given no origin. The solar wave-lengths of these were adopted and used in the reduction of the wave-lengths of the remaining lines.

The table at the end of the paper gives the residuum of lines after the elimination of those due to other metals. There can be little doubt that the majority of the lines, except, perhaps, some of the very lowest intensity, really belong to scandium. Exner and Haschek's wave-lengths and intensities of the scandium arc lines are given for comparison.

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* 'Öfversigt k. Vetensk. Akad. Forhandl.' (1881).

† Wellenlängen Tabellen für Spektralanalytische Untersuchungen auf Grund der Ultravioletten Bogenspektren der Elemente,' Leipzig und Wien, Franz-Deuticke, 1904.

Scandium Lines in the Solar Spectrum.

Rowland, in his "Tables of Solar Wave-lengths," ascribes a small number of lines to scandium, but a comparison of the Kensington photographs of the arc spectrum of this element with the solar spectrum shows that in addition to these there are other solar lines nearly certainly due to the same element. The table gives the solar lines which, by a careful comparison of the metallic and solar spectra, have been considered to correspond, without any doubt, with scandium lines. In addition to these, there is a considerable number which agree closely in position with weak solar lines, but of their identity there is, perhaps, some doubt. In some cases the solar lines are so weak that it is impossible to establish their identity with scandium lines by direct comparison of the two spectra, the only guide being the close agreement in wave-length, and the relative intensity of the metallic and solar lines. In other cases it is doubtful whether the metallic lines are strong enough to account for the solar lines. In the table these lines are denoted by an asterisk, and must be accepted only provisionally as "possible" scandium-solar lines.

The following analysis of the scandium lines, with reference to their intensities, and their appearance or non-appearance in the solar spectrum, will be of interest.

Intensity (Sc. arc lines).	Total number of Sc. lines.	Number undoubtedly represented in solar spectrum.	Number possibly represented in solar spectrum.	Number apparently absent from solar spectrum.
10	4	4	—	—
9	3	3	—	—
8	7	6	1	—
7	4	3	1	—
6	5	2	1	2
5	7	3	4	—
4	15	6	3	6
3	21	—	5	16
2	28	—	2	26
1	16	—	—	16

It will be seen that of the 23 lines of intensity 6 or greater, 18 occur in the solar spectrum, three others are doubtfully present, while two appear to be lacking. Of the lines below intensity 6, the great majority are missing from the Fraunhoferic spectrum.

Scandium Lines and the Chromospheric Spectrum.

The scandium lines which occur in the chromospheric spectrum, though not so numerous as those in the solar spectrum, are of considerably greater prominence. The strongest line of scandium at λ 4247·00 is very well developed in the chromosphere, and is, as far as the metallic lines are concerned, inferior only to the lines of strontium and calcium. Although all the scandium lines represented in the chromosphere have high intensities in the scandium arc spectrum, there are a few others of equal prominence in the metallic spectrum which are either lacking or occur only as quite insignificant lines in the chromospheric spectrum.

Chromospheric Lines probably due either wholly or partially to Scandium.

Chromospheric line.		Scandium line.			Remarks.
λ.	Intensity. Max. 10.	λ.	Intensity. Arc. Max. 10.	Intensity. Spark. Max. 10.	
4247·0	7	4247·00	10	10	Due solely to scandium.
4314·0	2	4314·25	9	8	" "
4321·2	5	4320·90	9	6	Probably partially due to *p*Ti 4321·20.
4374·9	7	4374·65	8	6	Probably partially due to *p*Ti 4374·90.
4399·9	5—6	4400·56	8	5	Probably partially due to *p*Ti 4399·94.
4670·8	3—4	4670·59	7	4	Due solely to scandium.
5031·2	2	5031·20	8	3	" "
5527·6	6	5527·03	10	7	This chromospheric line is broad and is probably composed of the scandium line and the strong Mg spark line λ 5528·64.

Scandium Lines in Sun-Spot Spectra.

Between F and D, the region over which the Kensington observations of sun-spot spectra extend, there are nine solar lines which have been found to be due to scandium, either wholly or partially. Of these, five occur amongst the most widened lines observed during the last 24 years. Four of them, however, have only been recorded a few times. The remaining one, λ 5672·047, is a very persistent widened line and is nearly always greatly affected. It is, of course, quite possible that the solar line in question, although weak, may be a compound one, and that an additional chemical element is involved in its formation. No origin other than scandium has been suggested by Rowland, and no alternative origin has been found for it by reference to Kensington spectra of metals. It must, therefore, be accepted provisionally as being really due to scandium.

Scandium Lines in Stellar Spectra.

It is quite probable that, as the stronger scandium lines occur in the solar spectrum, they also appear in the spectra of stars resembling the sun, such as those of the Aldebarian and Arcturian types. The closeness of the lines in these stars with the dispersion usually employed on stellar spectra makes it difficult to establish definitely whether the scandium lines are really present. At the next higher stage (Polarian, *e.g.*, γ Cygni) those scandium lines previously given as occurring in the chromospheric spectrum—at least, those in the ordinary photographic region, say λ 3900 to λ 4700—occur as well marked lines, as has been shown in a previous paper.*

At the next higher stage Cygnian (α Cygni) the only line which can with certainty be ascribed to scandium is that at λ 4247·00, corresponding to the strongest line of the element. Its stellar intensity, has, however, decreased considerably from that of the Polarian stage. At the higher stages represented successively by Rigelian (β Orionis), Taurian (ζ Tauri), Crucian (γ Orionis), and Alnitamian (ζ Orionis) types scandium lines are entirely lacking.

The photographs of the metallic spectra involved in the discussion were taken by Mr. C. P. Butler, A.R.C.Sc.

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* 'Phil. Trans.,' A, vol. 201, p. 205.

Arc Lines of Scandium.

* = Doubtfully identical with solar lines.

Kensington.		Exner and Haschek.		Corresponding solar lines.		Rowland's origin for solar lines.
λ.	Int. Max. 10.	λ.	Int. Max. 50.	λ.	Int.	
3907·62	10	3907·69	30	3907·62	3	Sc-Fe
11·94	10	12·03	30	11·96	2	Sc
		15·09	1			
		18·36	1			
		23·64	1			
		33·59†	6			
		52·43	1			
		89·18	1			
* 96·75	5	96·79	15	96·68	00	Sc
4014·66	3	4014·68	6			
20·55	8	20·60	20	4020·55	1	Sc
		23·36	1			
23·88	8	23·88	30	23·83	2	Sc
		31·51	2			
34·35	2					
36·98	1					
43·97	2					
46·64	2					
47·97	4—5	47·98	10	47·96	0	—
		50·09	2			
		52·00	1			
* 54·68	3	54·71	10	54·71	00	Sc
		56·72	3			
		67·15	2			
		75·13	2			
		78·70	2			
82·59	6	82·60	15	82·59	3	Fe-Sc-Ti
		86·15	1			
86·67	2—3	86·80	3			
87·26	1	87·28	3			
* 94·85	2—3	95·03	1	94·85	0	—
4106·02	2—3					
33·10	2	4133·10	4			
* 40·42	2—3	40·42	5	4140·40	0	—
41·78	1					
52·50	3	52·51	8			
62·85	1					
63·77	1					
65·38	2—3	65·39	8			
71·47	1—2					
71·98	2—3	71·92	2			
		4218·43	1			
		19·90	1			
4224·32	1					
		25·76	1			
		32·13	1			

† Possibly masked in Kensington photograph by K line of Ca.

Arc Lines of Scandium—*continued.*

Kensington.		Exner and Haschek.		Corresponding solar lines.		Rowland's origin for solar lines.
λ.	Int. Max. 10.	λ.	Int. Max. 50.	λ.	Int.	
		4233 ·83	2			
		37 ·96	1			
4238 ·25	2	38 ·21	3			
		39 ·72	1			
		46 ·27	1			
47 ·00	10	47 ·02	50	4247 ·00	5	Sc
		51 ·22	1			
		83 ·71	1			
		86 ·71	1			
* 94 ·91	4—5	94 ·94	5	94. 94	2	Zr
4305 ·83	4—5	4305 ·89	8	4305 ·87	2	—
14 ·25	9	14 ·31	30	14 ·25	3	Sc
20 ·90	9	20 ·98	20	20 ·91	3	Sc
25 ·15	8	25 ·28	20	25 ·15	4	Sc
54 ·74	3—4	54 ·79	3	54 ·78	1	—
		58 ·85	1			
		59 ·25	1			
74 ·65	8	74 ·69	20	74 ·63	3	Sc
84 ·99	4	84 ·98	3	84 ·99	0	Sc
		89 ·76	1			
4400 ·56	8	4400 ·63	20	4400 ·56	3	Sc
15 ·72	7	15 ·78	20	15 ·72	3	—
* 20 ·82	1—2	20 ·84	1	20 ·83	00	—
* 31 ·56	2—3	31 ·52	2	31 ·53	0	—
		4542 ·74	1			
		44 ·86	1			
		57 ·45	1			
*4563 ·40	2	—	—	4563 ·41	00	—
		74 ·20	2			
		4604 ·88	1			
4670 ·59	7	70 ·59	5	4670 ·59	2	Sc
		4709 ·53	1			
		29 ·43	2			
*4729 ·39	3	29 ·40	1	4729 ·38	0000	—
* 34 ·31	3—4	34 ·31	3	34 ·28	1	Fe ?
37 ·88	4	37 ·86	3			
* 41 ·24	5	41 ·23	4	41 ·26	1	Fe ?
* 44 ·04	6	44 ·01	5	44 ·01	000	—
		Exner and Haschek's record stops here.				
4820 ·52	2—3					
37 ·27	2—3					
4937 ·29	2—3					
54 ·12	1—2					
80 ·49	1					
87 ·26	1—2					
92 ·06	1—2					
5009 ·68	2					
31 ·20	8	—	—	5031 ·20	8	—
64 ·85	2					
70 ·34	3—4					

Arc Lines of Scandium—*continued.*

Kensington.		Exner and Haschek.		Corresponding solar lines.		Rowland's origin for solar lines.
λ.	Int. Max. 10.	λ.	Int. Max. 50.	λ.	Int.	
5075 ·85	1—2					
79 ·79	1					
81 ·68	6					
83 ·77	5					
* 85 ·64	4	—	—	5085 ·67	0	—
87 ·06	3					
87 ·18	2					
89 ·95	2					
96 ·81	2					
99 ·28	3—4					
5101 ·21	2					
04 ·43	1					
05 ·60	2—3					
09 ·09	1					
10 ·85	<1					
12 ·87	1					
16 ·73	2					
21 ·60	1					
31 ·14	<1					
47 ·08	2					
48 ·28	2					
5239 ·99	5—6	—	—	5239 ·99	1	—
58 ·46	2—3					
69 ·65	1—2					
85 ·88	2					
5307 ·83	1					
18 ·41	2					
25 ·14	2					
28 ·05	1					
49 ·32	3					
56 ·14	3—4					
58 ·69	2—3					
89 ·89	1—2					
92 ·12	3					
5478 ·66	2					
82 ·18	4					
* 84 ·81	3—4	—	—	5484 ·85	000	—
5514 ·40	4					
* 20 ·70	4—5	—	—	5520 ·73	00	—
27 ·03	10	—	—	27 ·03	3	—
91 ·44	2					
5658 ·10	7	—	—	5658 ·10	2	Y
58 ·56	3—4	—	—	58 ·56	0	—
67 ·40	3—4	—	—	67 ·37	0	—
69 ·25	4	—	—	69 ·26	1	—
72 ·05	9	—	—	72 ·05	0	Sc
84 ·44	4	—	—	84 ·42	1	—
* 87 ·07	8	—	—	87 ·06	000	—
*5700 ·38	7	—	—	5700 ·40	00	—
11 ·98	6					
17 ·54	3					

"On the Stellar Line near λ 4686." By Sir NORMAN LOCKYER, K.C.B., LL.D., Sc.D., F.R.S., and F. E. BAXANDALL, A.R.C.Sc.

Received January 4,—Read February 9, 1905.

[PLATE 13.]

In the publication of the results derived from a study of the Kensington photographic spectra of the 1898 eclipse, it was stated[*] that a fairly prominent line recorded near λ 4686, for which no terrestrial origin could be found, agreed closely in position with a well-marked line of unknown origin in one of the Kensington photographs of the spectrum from a helium tube. In the helium photograph the position has been recently found from careful measures made on the lines 4120·97, 4388·10, 4713·25, and the line in question, and subsequent use of Hartmann's formula.

The resulting wave-length of the strange line was 4685·97. Similar measurements were made on the eclipse photographs, the fiducial lines used being 4508·5 (*p* Fe), 4584·0 (*p* Fe), and 4713·25 (He). The result gave 4685·90.

The two calculated wave-lengths so nearly agree that it is very probable the line is of identical origin in the two cases. The eclipse line is, moreover, of the same nature as the helium eclipse lines, long and sharply defined. It would therefore seem that the line is due to a gas which is associated in some way with helium. The line, however, only appears in one photograph of the helium spectrum, and whether this is due to the particular sample of helium used, or to some special condition of current which is conducive to the appearance of the strange line, it is impossible to say.

A line near the same position has been recorded by various spectroscopists in different celestial spectra. The following table contains the available records of the line in question :—

Spectrum.	Observer.	λ.
Bright line stars	**Campbell**	**4688**
" "	**Pickering**	**4688**
" "	**McClean**	**4687 ·5**
Nebulæ	**Campbell**	**4687**
Orion stars	**Pickering**	**4685 ·4**
ε Orionis	**Lockyer**	**4687 ·0**
Trapezium star (Bond 628)	**Keeler**	**4686 ·4**
β Crucis	**McClean**	**4686 ·1**
Chromosphere	**Evershed**	**4685 ·7**
"	**Lockyer**	**4687 ·0**
"	**Frost**	**4685 ·7**
"	**Lord**	**4686 ·3**
"	**Humphreys**	**4685 ·4**
	Mean λ ..	**4686 ·4**

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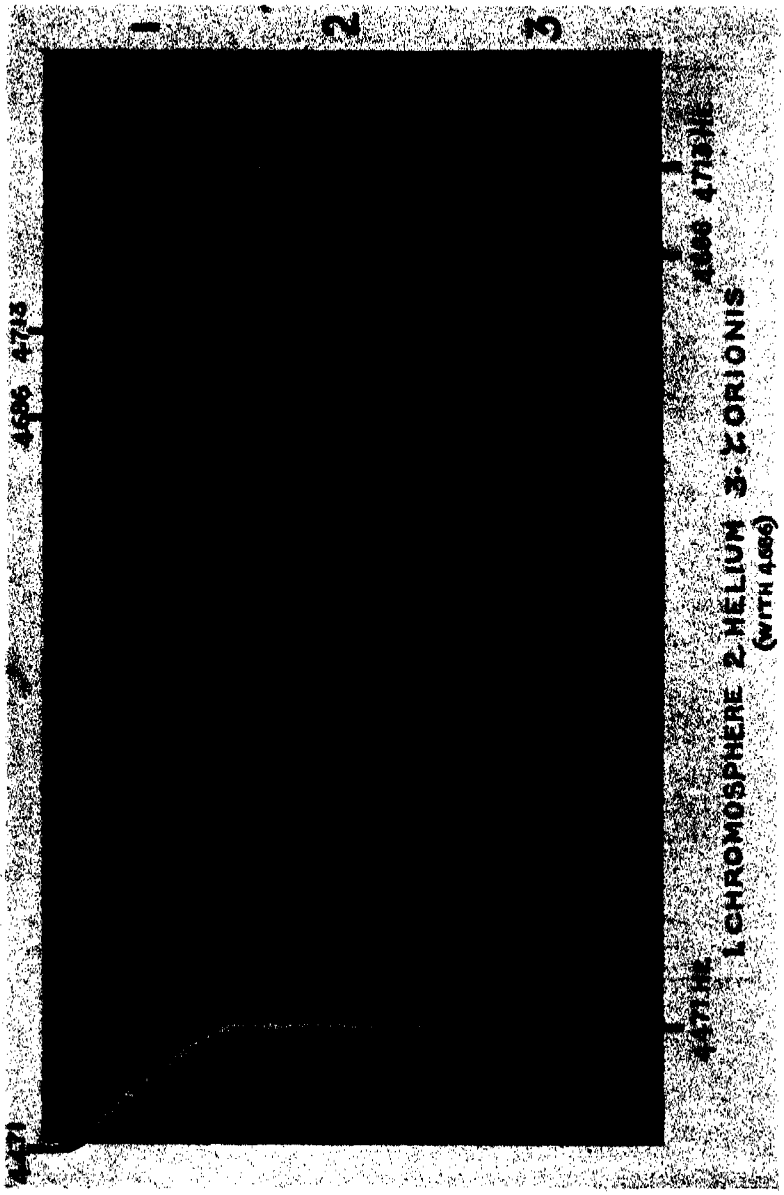
[*] 'Phil. Trans.,' A, vol. 197, p. 202.



1. CHROMOSPHERE 2. HELIUM 3. ζ ORIONIS (WITH 4686)

It will be seen that the mean wave-length is in fairly good accord with that of the unknown terrestrial line 4685·97. The line, however, in the nebular and bright-line-star spectra is broad and ill-defined, and the estimated wave-lengths are probably somewhat uncertain, and not to be depended on so much as those obtained from spectra in which the line is sharply defined. If in seeking the mean wave-length these probably less accurate wave-lengths be excluded, the result is 4685·9, which is in very close agreement with the position of the terrestrial line.

Rydberg has shown that the stellar line near 4686—associated with the new series discovered by Pickering in the spectrum of ζ Puppis—is probably the first line of the principal series furnished by hydrogen. His calculated wave-length value for the line is 4687·88,* which would appear to be about two tenth-metres in error, as the corresponding celestial line probably has, as is shown in the present note, a wave-length near 4685·9.

In the light of this evidence for the probable identity of the terrestrial and stellar lines, it seems desirable to institute further research on the spectrum of helium under varying electrical conditions, with the object of possibly obtaining the terrestrial equivalents of the so-called new hydrogen series of ζ Puppis.

DESCRIPTION OF PLATE.

The plate shows a comparison of the spectrum (region 4450 to 4750) of the chromosphere, the helium spectrum containing the line 4686, and that of ζ Orionis (Alnitamian). The identity of position of the helium lines, and 4686, with lines in the chromospheric and stellar spectra is clearly shown. The fainter lines in the helium spectrum are all due to oxygen.

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* 'Ast. Phys. Jour.,' vol. 6, p. 237.

"Note on the Spectrum of μ Centauri." By Sir NORMAN LOCKYER, K.C.B., LL.D., Sc.D., F.R.S., and F. E. BAXANDALL, A.R.C.Sc.

Received January 4,—Read February 9, 1905.

An investigation of Pickering's reproduction of this spectrum*—which apparently consists of the spectrum of an Orion star + bright hydrogen lines and certain other bright lines of minor intensity—suggested that the latter are radiation lines corresponding to some of the stronger absorption lines of α Cygni. These α Cygni lines have previously been attributed to the enhanced lines of certain metals, chiefly Fe, Ti, Cr, Mg, and Si.

A close investigation has now shown that nearly all the most marked bright lines in μ Centauri—other than those of hydrogen—occupy positions closely corresponding to those of the most conspicuous enhanced lines of iron. The wave-lengths of some of the bright μ Centauri lines are compared with those of the enhanced lines of iron and α Cygni lines in the table at the end of this note. The close agreement is very noticeable.

It is worth while, then, to analyse in detail Pickering's statement in his note† on the μ Centauri spectrum. He states: "Lines 4922·1 and 5015·8 are bright on the edge of greater wave-length." The lines whose wave-lengths he gives are the helium-Orion absorption lines. The only two enhanced iron lines in this region are at λλ 4924·11 and 5018·63, which occupy exactly the positions relatively to the helium lines which Pickering notes as being bright in the μ Centauri spectrum—that is, they border the helium lines on the edge of greater wave-length.

Again, he says: "The two most conspicuous (bright lines) are at wave-lengths 4232 and 4584 approximately." Two of the most marked lines in the α Cygni spectrum are at λλ 4233·25 and 4584·02, and these undoubtedly correspond to the two most conspicuous enhanced lines of iron between H_δ and H_β.

Again. "Line 4387·8 is bright on the edge of shorter wave-length." In α Cygni there is a well-marked line at λ 4385·55, which agrees in position with another enhanced iron line.

Also: "A diffuse bright band appears on the side of shorter wave-length of the dark line 4531·4." There is a distinctive group of α Cygni—enhanced iron lines at λλ 4508·46, 4515·51, 4520·40, 4522·69, which, thrown together into an irresolvable group in μ Centauri, may well correspond to the diffuse line quoted by Pickering.

Further: "The dark line 4553·4 is superposed on a bright band."

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* 'Annals Harv. Coll. Obs.,' vol. 28, Part II, Plate 1.

† 'Annals Harv. Coll. Obs.,' vol. 28, Part II, p. 178.

Bright Lines in the Spectrum of μ Centauri.

λ (μ Centauri).	Nature.	Probable origin.	λ of probable origin.	α Cygni.		Remarks.
				λ.	Intensity (Max. 10).	
4171·4 to 4181·4	Bright and broad	*p* Fe	4173·52 4178·95	4173·5 4179·0	6—7 6—7	Mean position of Fe double 4176·2, that of the μ Centauri line 4176·4.
4232·9	Very bright and narrow	*p* Fe	4233·25	4233·3	8	
4295·7 to 4303·1	Bright but not well-marked	*p* Fe	4296·65 4303·34	4296·7 4303·3	4 5	Mean position of Fe double 4299·9, that of μ Centauri line 4299·4.
4385·0	Bright and narrow	*p* Fe	4385·55	4385·5	5—6	
4508·9	" "	*p* Fe	4508·46	4508·5	5	
4515·1	" "	*p* Fe	4515·51	4515·5	5	
4518·6 to 4527·6	Bright but irresolvable	? *p* Fe + extra line	4520·40 4522·69	4520·4 4522·7	4 5	Mean position of *p* Fe double 4521·5, that of μ Centauri line 4523·3.
4549·9	Bright and narrow	*p* Fe	4549·64	4549·8	7	
4556·3	" "	*p* Fe	4556·06	4556·1	5	
4584·6	Very bright	*p* Fe	4584·02	4584·0	7	

This bright band may very well correspond to the α Cygni enhanced iron lines 4549·64 and 4556·06 thrown together in the μ Centauri spectrum. It is possible, though, that the dark line 4553·4, quoted by Pickering, is only the dark interspace between the bright 4549·64 and 4556·06 lines.

It may be here remarked that among the brightest lines in the spectra of Novæ at their initial stages are lines agreeing in position with the most marked α Cygni and enhanced Fe lines, and in this way we trace a resemblance between the minor bright lines of μ Centauri and the most conspicuous bright lines—other than those of hydrogen—in the early spectra of Novæ.

Lines corresponding to these bright lines in μ Centauri also occur in the spectrum of γ Cassiopeiæ, but they are far less well-defined in the case of the latter star.

The wave-lengths of the μ Centauri lines given in the table were reduced, by means of Hartmann's formula, from measures made on Pickering's reproduction, the fiducial lines used being 4121·0 (He), H_γ, and H_β.

"On Europium and its Ultra-violet Spectrum." By Sir WILLIAM CROOKES, D.Sc., F.R.S. Received January 26,—Read February 9, 1905.

Europium was discovered in 1901 by Demarçay,* accompanying samarium, from which he separated it by fractional crystallisation of the double nitrates of magnesium and the earths. Demarçay considered that his new earth was identical with De Boisbaudran's $Z\epsilon$ and $Z\zeta$, and was the same which I had announced in 1885† as giving an extremely sharp red line in the phosphorescent spectrum at wave-length 609—an earth which in 1889‡ I said was a new one, and designated by the name of $S\delta$. I detected the earth $S\delta$ during an examination of the phosphorescent spectra given by some of the fractions of samaria and of yttria, neither of the earths being pure.

Europium is the first member of the terbium group, gadolinium being the second member. On the other side it comes next to samarium, the last member of the cerium group. Assuming the oxide of europium to be Eu_2O_3, the element has an atomic weight of 151·8, from the analysis of its sulphate, $Eu_2(SO_4)_3,8H_2O$.

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* 'Comptes Rendus,' vol. 132, p. 1484, and 'Chemical News,' vol. 84, p. 1

† 'Phil. Trans.,' vol. 176, p. 691.

‡ 'Journ. Chem. Soc.,' vol. 55, pp. 250—285.

MM. Urbain and Lacombe* have sharply separated europium from samarium in the manner outlined by them in my note on gadolinium† by fractional crystallisation of the double nitrates of bismuth or magnesium with the nitrates of the rare earths. I owe to the kindness of M. Urbain a sufficient quantity of the oxide of europium to enable me to obtain a good series of its photographed spectrum, a copy of which accompanies the present paper. (Not reproduced.)

Exner and Haschek have measured the wave-lengths of the europium lines‡ from material supplied by Demarçay. A comparison of their lines with mine shows that the material was by no means pure.

Urbain's europia is not quite so free from impurities as his gadolinia. I have been able to detect in my photographs the following lines:—Gadolinium is represented by very faint lines at 3450·55, 3481·99, 3585·10, 3646·36, 3654·79, 3656·32, 3664·76, 3697·90, 3699·89, 3743·62, 3768·52, 3796·58, 3805·70, 3850·83, 3851·16, 4050·08, 4225·33. Yttrium is represented by the line at 3774·51, lanthanum by the line at 3988·66, and calcium by the two lines at 3933·825 and 3968·625.

No lines of bismuth or magnesium are to be seen.

Most of the lines of impurities are exceedingly faint, showing that the impurity is only present in very minute proportion. Indeed, I have only mentioned them if they correspond with strong lines in the gadolinium or other spectra. Both in the europium and the gadolinium spectrum I have not attempted to give wave-lengths of all the excessively faint lines. If at some future time it becomes of interest or value to ascertain their wave-lengths, all the necessary data are present whereby they can be identified.

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* 'Comptes Rendus,' vol. 138, pp. 84, 627, 1166; 'Chemical News,' vol. 89, pp. 53, 179, 277.

† *Supra*, p. 420.

‡ 'Wellenlängen-Tabellen für Spektralanalytische Untersuchungen,' F. Deuticke, Leipzig und Wien, 1902.

"On a Relation between Autumnal Rainfall and the Yield of Wheat of the Following Year.—Preliminary Note." By W. N. SHAW, Sc.D., F.R.S., Secretary of the Meteorological Council. Received February 2,—Read February 2, 1905.

By autumn, in this note, is to be understood the period from the 36th to the 48th week, both inclusive, of the year, as represented in the *Weekly Weather Report* of the Meteorological Office; it covers the months of September, October, and November, approximately. The rainfall to be referred to is the average amount in inches, for the "Principal Wheat Producing Districts," for the period mentioned, in successive years. The amounts are taken from the summaries of the *Weekly Weather Report.*

The yield of wheat is that given for successive years in the annual summaries of the Board of Agriculture and Fisheries as the average yield in bushels per acre for England, since 1884, or more strictly since 1885, as that is the first year for which the figures for England are given separately. In 1884 the figure for Great Britain, which generally differs but little from that for England, is used.

These are the only figures in the official publications which are immediately available for the purposes of comparison. The totals of rainfall for the 13 weeks have been compiled from the weekly amounts, otherwise the figures are taken as they stand in published returns. The areas referred to are not exactly coterminous, but they are more nearly so than if the rainfall values had been taken for the whole of England, or the wheat yield for Great Britain.

When the autumn rainfall and the yields of wheat for successive years from 1884 to 1904, as thus defined, are plotted, the rainfall curve being inverted, *i.e.*, rainfall being measured downward on the paper while yield is measured upward, there is a very striking similarity between the curves, so much so as to suggest that if the scales were suitably chosen the two curves would superpose and show general consonance, with exceptions, more or less striking, in a few of the years. In other words, the yield of wheat in any year seems to depend mainly on the absence of rainfall in the previous autumn, and but little on any other factor.

The obvious algebraical expression for such a condition as the curves represent is a linear equation, and the equation which represents the relation between yield of wheat for England and the previous autumn rainfall is:—

Yield = 39·5 bushels per acre − 5/4 (previous autumn rainfall in inches).

If we call the yield obtained from the rainfall by this equation the "computed yield," a comparison with the actual yield for the 21 years shows that the computed yield agrees with the actual yield within half a bushel in 7 years out of the 21. In 14 years the agreement is within 2 bushels; in the remaining 7 years the difference between computed and actual yield exceeds 2 bushels. The extreme variation of yield in the 21 years is 9 bushels, from 26 bushels per acre in 1892 and two other years, to 35 bushels per acre in 1898.

Of the 7 years for which the formula gives yields differing from the actual by upwards of 2 bushels, 1896 is the most conspicuous, its actual yield exceeds the computed yield by 4·5 bushels.

These 7 years all show anomalous seasons. Taken *seriatim*, they are 1887, 1888, 1893, 1895, 1896, 1899, and 1903.

In 1888 and 1903 the crops were washed away by 10 inches of rain in the summer; 1893 is the year of phenomenal drought and the crop was below the computed figure by 2·5 bushels. The years 1892 and 1899 are interesting, because though the amounts of rain were up to the average, the former had 8 dry weeks and the latter 10 dry weeks out of the 13 included in the conventional autumn. They were thus dry autumns, the average amount of rainfall being made up by a few exceptionally wet weeks. The yields correspond with dry autumn values. They are above the average and above the computed figures by some 2 or 3 bushels per acre.

There remain 1895 and 1896. 1895 was the year of remarkably cold weather, and in that year the yield fell short, but in the following year the deficiency was made up by a yield as much above the computed value as the previous one fell short. It would appear that in this instance the productive power not utilised in the year of the great cold was not lost but stored. On the other hand, it must be remarked that 1896 had the advantage of a specially dry winter.

It appears from these considerations that the dryness of autumn is the dominant element in the determination of the yield of wheat of the following year. The averages of yield and of rainfall are taken over very large areas, and it may be taken for granted that the investigation of the question for more restricted areas would introduce some modification in the numerical coefficients, if not in the form of the relation.

The data for making such an investigation are not yet in an available form. A comparison has been made between autumnal rainfall for "England, East" and the average yield for the counties of Cambridge, Essex, Norfolk and Suffolk, which shows a similar relation but a magnified effect of autumnal rainfall upon the crop, and also two exceptional years which have not yet been investigated.

"The Ascent of Water in Trees." By ALFRED J. EWART, D.Sc., Ph.D., F.L.S., Lecturer on Botany in the University of Birmingham. Communicated by FRANCIS DARWIN, For. Sec. R.S. Received November 2,—Read December 1, 1904.

(Abstract.)

As the result of a series of experimental observations bearing upon this problem, the author has been led to the conclusions stated in brief below.

The flow of water through open vessels filled with sap takes place in accordance with Poiseuille's formula for the flow through rigid cylindrical tubes, divergences being due to the presence of irregular internal thickenings in the vessels, and to local constrictions or deviations from the circular outline.

Hence the velocity of flow is directly proportional to the pressure and to the square of the radius of the tube, inversely proportional to the length of the tube and to the viscosity of the liquid. A small number of large vessels, therefore, offer very much less resistance to flow than a large number of narrow ones having the same length, and the same total internal area of cross-section. Since viscosity is largely dependent upon temperature, the latter forms an important factor in regulating the flow, the viscosity and the resistance falling with a rise of temperature.

With an average rate of flow the total resistance due to the viscosity of the water flowing through the vessels is always less, and in climbing plants with large vessels is considerably less, than a head of water equal in height to the stem. The adult vessels of actively transpiring Angiospermous trees always contain air-bubbles, and these introduce a resistance to flow which is inversely proportional to the radius of the tube, when the air-bubbles and water-columns move together. When the air-bubbles are comparatively stationary, as in most vessels, the resistance is still further increased, and it becomes very great when the vessels are small and the air-bubbles numerous. In intact vessels containing air the rates of flow under similar pressures are proportional to a power of the radius lying between 1 and 2, the volume passing to a power of the radius lying between 2 and 4.

Estimations of the amount of flow, made from the rate of flow and the diameters and number of the vessels, showed that the actual flow takes place in the wood of Dicotyledons almost entirely through the cavities of the vessels and hardly at all through the tracheides. In young stems saturated with water under pressure, a considerable flow takes place through the pith, but practically none in intact transpiring stems.

In a cut stem, apart from the blocking at the cut surfaces, a gradual diminution of conductivity occurs along its entire length after water has been passed through for some time. This appears, in part at least, to be due to the development of micro-organisms in the vessels, but may be aided by swelling, by lessened permeability, or by other changes in their walls.

The length of the vessels in the wood of the branches examined averages from 7 to 36 centimetres, the tracheides of the yew being from 0·2 to 0·5 of a centimetre in length. Since, however, the vessels appear mainly to end at the nodes where branches arise, it is possible that they may be much longer in the young wood on old bare trunks. The resistance to transverse flow through saturated wood is 800 to 45,000 times greater than to longitudinal flow, the resistance to filtration under pressure through a single partition wall being from 2 to 10 times greater than that to the flow through the entire length of a vessel filled with water in the wood of a crab apple.

The total resistance to flow in the erect stems of actively transpiring plants appears to correspond to a head of water of from 6 to 33 (shrubs and small trees), or from 5 to 7 (large trees) times the height of the plant. Hence in the tallest trees the total pressure required to maintain active transpiration may be equivalent to as much as 100 atmospheres.

No leaf could produce or maintain an osmotic suction of this intensity, and in the presence of large air-bubbles in the vessels the stress transmitted in them from the leaves could never be as great as an atmosphere. Vines* found, for instance, that the suction force of a transpiring branch was never greater than two-thirds of an atmosphere. The supposition that these forces might summate is entirely erroneous. On the contrary, the leaves at the base of a tree would pull water down from the upper vessels and leaves, instead of up from the roots, in the absence of any pumping action in the stem, and of any root-pressure.

If the air-bubbles in the vessels were exceedingly minute, they might be under a small positive pressure, while the water outside was under a maximal strain of five atmospheres. This would suffice to overcome the resistance offered during active transpiration by 30 to 80 feet of stem, hence the results obtained by Strasburger with dead stems. The maximal osmotic suction exercised by the leaves, as determined by comparing the osmotic pressures during active transpiration of the leaves at the top and bottom of an elm 18 metres high, appears to be from 2 to 3 atmospheres, and is usually less than this. At the same time the total resistance to flow in the trunk of this tree would be from 10 to 12 atmospheres.

It appears, therefore, that to maintain flow, a pumping action of some kind or other must be exercised in the wood, for which the presence of active living cells is essential. In support of this it has been shown that the production of wood in a slowly growing tree is greater than is necessitated by mechanical requirements. In other words, the production of new wood is largely determined by the length of time during which the wood-parenchyma can remain active.

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* 'Annals of Botany,' 1896, vol. 10, p. 438.

There is no known means by which these cells can directly pump water in a definite direction, although the existence of a power of absorbing and exuding water under pressure has been empirically determined to exist in the living wood of cut branches. It is suggested that the wood-parenchyma cells by the excretion and re-absorption of dissolved materials may bring into play surface-tension forces within the vessels of sufficient aggregate intensity to maintain a steady upward flow, and to keep the water of the Jamin's chains in the vessels in a mobile condition ready to flow to wherever suction is exercised upon it.* The rapid rates of diffusion required for such action do actually exist in the wood-parenchyma cells.

It appears that the terminal branches of trees at heights of from 22 to 44 feet above ground exhibit little or no power of bleeding in spring. Possibly in such trees the pumping action is only used or developed in the wood of the older stems, or is only exercised when transpiration is active, and when the water-columns in the vessels attain a definite size relatively to the wood-parenchyma cells. The importance of the Jamin's chain in the vessels is that it renders a staircase pumping action possible, and enables the water to be maintained in the vessels in a labile condition, ready to flow to any point where moderate suction is exercised. This pumping action being diffused and probably regulated, need not produce any high pressure of exudation at the terminal branches of tall trees, which, in fact, appears always to be absent at high levels.

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* Surface-tension actions would be possible in the absence of air-bubbles wherever the wood-parenchyma cells contained oil or any other substance non-miscible with water, as they often do.

"Further Observations on Slip-Bands in Metallic Fractures.—Preliminary Note." By WALTER ROSENHAIN, B.A., B.C.E.

Communicated by Professor EWING, F.R.S. Received February 9,—Read February 16, 1905.

[PLATE 14.]

The main purpose of the present paper is to describe what the author believes to be a novel method of investigating the micro-structure of metals, and to give some account of preliminary results obtained by its aid. The method was devised in order to throw further light on the true nature of slip-bands, and the preliminary results relate mainly to this question. The investigation described in this paper is thus a further development of researches carried out in the first place by Professor J. A. Ewing, F.R.S. and the author jointly ("The Crystalline Structure of Metals," Bakerian Lecture, 1899),* and subsequently by the present author alone ("The Plastic Yielding of Iron and Steel.")† In the course of correspondence on the latter paper, M. F. Osmond drew the attention of the author to certain experimental facts concerning the behaviour of slip-bands under oblique illumination, which had formerly escaped attention. The difficulty met with in convincing M. Osmond of what the author believes to be the true interpretation of these phenomena has led him to seek another means of examining the character of slip-bands, which should not be based upon the interpretation of effects of illumination.

A direct means of examining the surface configuration of a piece of metal upon which slip-bands have been produced would be presented by a transverse section of such a specimen, provided that the section could be produced with an absolutely sharp edge, and that the sectional elevation of the features in question were large enough to be visible under the microscope. The difficulties in the way of obtaining a section even approximately satisfying the first of these conditions are, however, considerable. No useful result can be obtained by cutting the specimen through and simply polishing the exposed section. It is a well-known fact that the extreme edges of specimens prepared by the usual methods of polishing are always more or less rounded off, so that it becomes impossible to focus upon any definite edge with high-power lenses; and even apart from this defect, there would be no guarantee that the edge represented a true section of the pre-existing surface, since the processes of cutting, grinding, and polishing would probably fray out the edge and remove some of the weaker or more delicate features. In some departments of optics a somewhat similar problem is met with, and is satisfactorily overcome by embedding the glass in pitch, supported by other pieces of glass.

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* 'Phil. Trans.,' A, 1899, vol. 193, pp. 353 to 375.

† 'Journal of the Iron and Steel Institute,' 1904, pp. 335 to 390.

The author has adopted this principle of supporting the surface, which in section becomes the edge, by means of an adherent layer of hard material; but the conditions which such a layer must satisfy for the purposes of metallography are very stringent. The adherent layer should be of approximately the same hardness as the metal under examination. It must adhere to it with extreme closeness, and with strength enough to resist the processes of cutting, grinding, and polishing; there must be no chemical action on the surface of the metal specimen, and the adherent layer must be free from grit, which would prevent the polishing of the transverse section. Finally, it is desirable that the protecting layer should be attached without heating the specimen, as even moderate elevations of temperature frequently affect the micro-structure of strained metal. This last condition eliminates such substances as pitch or fusible alloys, which were, moreover, found unsatisfactory in other respects also. The difficulty of cutting and polishing eliminates the majority of cements and plasters. The author was therefore led to use a deposit of another metal obtained by electrolytic means, and this method has proved satisfactory.

The specimens used consisted of strips of the mildest steel, such as is used for transformer sheet, and after preparation an electro-deposit of copper was applied to them. By first bending the strips into a flat U shape, short portions of their length could be polished in the usual manner for microscopic examination; subsequently the strips could be readily strained and even broken in tension by means of an ordinary vice provided with clamping-plates attached to the jaws. The slip-bands and other features of the specimens having been satisfactorily observed, electro-deposition was proceeded with. The specimens could not be immersed directly in the usual acid solution of copper sulphate used in copper-plating, as the surface would have been attacked and spoilt by the action of simple substitution; they were accordingly first coated with a thin film of copper in a bath of copper cyanide under the action of a very weak current, and were only then removed to the usual bath where deposition could be carried on as rapidly as is consistent with the formation of a solid and coherent deposit. The copper deposit was generally allowed entirely to envelope the strips of iron, and deposition was carried on until a thickness of 4 to 5 mm. was reached. This occupied from 8 to 14 days.*

The specimens were then cut across, generally in a direction roughly parallel to the direction of the original tensile strain. In order to obtain a satisfactory polish, however, the ordinary method of polishing with emery papers, followed by rouge, had to be slightly modified; not only is it difficult to polish electro-deposited copper by means of rouge, but it was found that this polishing medium rapidly eroded a deep groove between the copper and iron, thus defeating the object of the method. After some trials, a satisfactory polishing medium for this and other purposes where surface erosion is undesirable was found in calcined oxide of magnesium. The powder, as purchased under the description of "chemically pure light oxide of magnesia," was used by the author without further treatment, but still better results could no doubt be obtained by using an elutriated product. The magnesia powder is used in much the same way as rouge; a revolving disc of metal is covered with several layers of fine well-washed calico, and fed with a thin paste of magnesia and water; it is, however, essential that only distilled water should be used, as the magnesia becomes gritty in the presence of dissolved salts. In any case, its use requires some care, as such a magnesia disc, if allowed to dry, becomes hard and useless.

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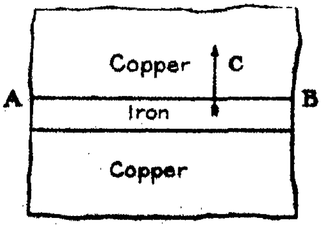
* The electro-deposition on the majority of the specimens here referred to was carried out by Mr. S. Field, at the Northampton Institute, London, and the author is greatly indebted to his skill and kindness.

The section, when satisfactorily polished by means of magnesia, is not yet ready for detailed examination; even when the grinding on emery has been carried so far that very little polishing is required, it is found that a considerable amount of metal has been smeared or dragged over the surface, more or less obliterating the true boundary line which it is desired to examine. In order to overcome this obstacle, it is advisable so to arrange matters that the last rubbing on emery paper shall be done in a direction approximately parallel to the boundary of the two metals; the direction of rubbing during the final polishing should then be at right-angles to the boundary, and the specimen should be so held on the revolving disc that the unavoidable tendency to drag or smear will be such as to draw the iron over the copper on the side where the boundary is to be examined.

Fig. 1 illustrates this point on an exaggerated scale; the diagram

Fig. 1.



represents the face of the section, AB representing the boundary between iron and copper which gives the sectional view of the previously prepared surface, while the arrow C indicates the proper direction of rubbing during the final polishing process.*

The film of metal smeared over the boundary under these circumstances is extremely thin,† and can be removed by slight etching, preferably by means of a reagent which dissolves the iron while leaving the copper untouched. Such a reagent is found in a 10-per-cent. solution of picric acid in alcohol, acting for about 30 seconds. This treatment leaves a clearly defined boundary line appearing under a certain incidence of "vertical" illumination as a narrow black line, and under other illumination being visible merely by the colour-contrast between the iron and copper. Even under the highest power of the microscope the boundary line can be seen sharply in focus, but it then becomes evident that there is always a very slight difference of level between copper and iron, and that the black line seen at the boundary under certain conditions of illumination is the shadow of the edge of the copper projected on the iron. As the copper is entirely unacted upon by the etching reagent, the edge of the copper may be taken as the true outline of the transverse section of the previously prepared surface.

When a previously polished and etched specimen of iron which has had slip-bands developed upon its surface by strain is treated and examined in this way, the boundary line shows well-marked steps or serrations, readily visible under a magnification of 1000 diameters. It was, however, necessary to show that these were really the sections of slip-bands, and were not due to any of the other processes gone through by the specimen, such as the initial etching of the prepared surface or the electro-deposition itself. For this purpose a series of test specimens were prepared and treated in a similar manner. The first of these had been polished in the initial stage, but neither etched nor strained, and the boundary in the transverse section showed an almost unbroken straight line, thus proving that the electro-deposition in no way produced irregularities on the boundary; in fact, the extreme closeness of adhesion of the deposit, and the accurate manner in which it follows the minutest details of the prepared surface, is a most remarkable feature of the whole process.

It was at first thought that the examination of such boundaries might throw light on the mode of adhesion of electrolytic deposits, but none of the features observed afford any evidence on that question. In a second specimen the initial surface had been polished and etched, but not strained, and here also there was an entire absence

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* The special process of polishing here described was worked out in conjunction with Mrs. W. Rosenhain, who entirely carried out its application.

† Mr. Beilby believes such surface films of metal to be transparent, but in the present instance, where one metal was smeared over the other, transparency would have been easily detected, but no evidence of its existence was found.

FIG. 2.

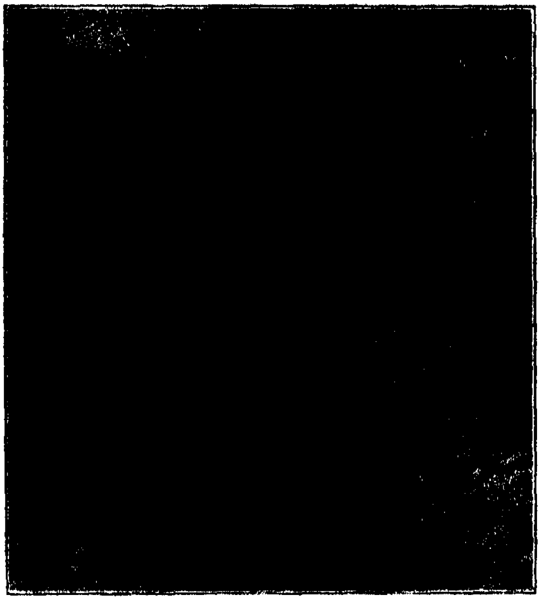
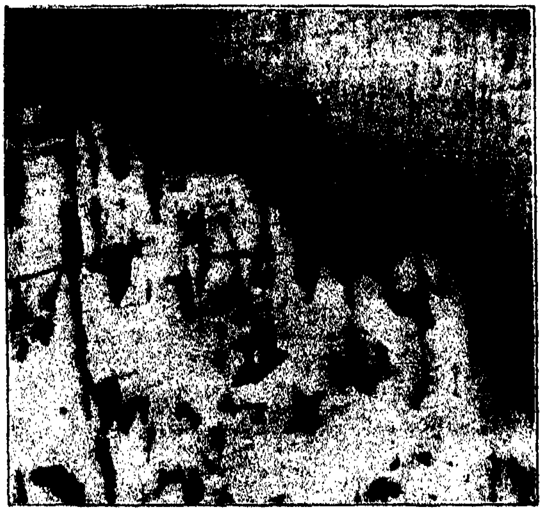


FIG. 4.



of steps or serrations in the boundary in the *transverse section.* Although the etching had been carried rather far, so that the outlines of the crystals on the initial surface were very well marked, yet the differences of level between adjacent crystals, which are one result of etching, were only barely visible on the transverse section. A third specimen was polished and strained without any preliminary etching, and examination of a transverse section showed steps and serrations in the boundary line similar to those found on specimens which had been etched before being strained, but they appeared to be somewhat smaller and slightly less well-defined.

It has thus been shown that these steps or serrations in the boundary line are found in previously strained specimens, whether etched or not, but that they are not found in unstrained specimens. The author therefore feels justified in concluding that the steps seen in transverse sections of strained specimens are the sectional views of slip-bands. Fig. 2 (Plate 14) is a photomicrograph of an example of these steps, under a magnification of 1000 diameters. It will be seen that the steps, although very minute, are perfectly distinctive, and that they could not be mistaken for generally rounded foldings of the surface; they possess, in fact, a general geometrical character, which the author regards as conclusive evidence that they are caused by slip on cleavage or gliding planes of the crystals, and not by any folding or crumpling of the metal. On the other hand, these steps as seen in section are so minute that it is not very safe to draw conclusions as to the *details* of their configuration; under the most critical conditions of observation, the upper edges of these steps do not appear to be sharply angular, but rather to be rounded off slightly, and in some cases they even appear to possess a minute crest or ridge. Such a configuration would readily account for some of the phenomena pointed out by Osmond, but the dimensions of these details are so near the limit of resolving power of the lenses used by the author (Zeiss 3 mm. apochromat. oil-immersion, 1·40 N.A.) that no great reliance can be placed upon their apparent shape, particularly as the tendency of microscopic vision is to obliterate minute angles whose dimensions lie near the limits of resolution.

In general terms, however, there can be no doubt that the sectional views of slip-bands obtained by the author strongly confirm the theory of deformation by slip, and in order to emphasise this confirmation the diagram, Fig. 3, is given for comparison with the photomicrograph,

Fig. 3.

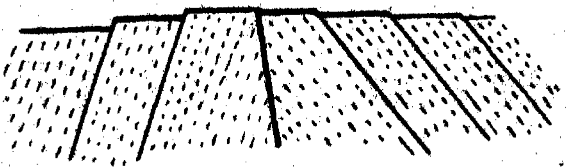


Fig. 2 (Plate 14). (The diagram is a replica of one originally used by Professor Ewing and the present author to illustrate their explanation of the character of slip-bands, see paper referred to above.) The change of direction of the steps on passing from one crystal to another, as indicated on the diagram, is readily observed on the actual sections.

The method above described of supporting the surface of a metal specimen by means of an electrolytic deposit so as to render possible the production of accurate transverse sections, is capable of application to a number of questions. The author is engaged in applying it to one of these, viz., the study of fractures produced in various ways. The difficulty of obtaining satisfactory sections of fractures has hitherto stood in the way of systematic investigation of the path taken by fractures; the photomicrograph, Fig. 4 (Plate 14), shows how the present method overcomes this difficulty; it represents a section through a "fibrous" fracture of a piece of very mild steel, under a magnification of 90 diameters. As compared with the sections of slip-bands, the details of such a fracture are very large, but even under the highest magnification the sharpness of the boundary is maintained, and it is even possible to follow the path of the fracture among the lamellæ of the pearlite in this steel. The investigation of flaws, of the edges and cuts of cutting tools are further examples of questions which can be investigated by the aid of the method here described.

Specimens of iron and steel for the experiments here described have been very kindly supplied to the author by Messrs. Joseph Sankey, of Bilston, and Messrs. Cammell, Laird and Co., Limited, of Sheffield. The cost of some of the apparatus and a portion of the expense of this investigation have been defrayed out of a grant from the Government Grant Committee of the Royal Society, and the author is also indebted in this connection to the Council of the Iron and Steel Institute for the award of an Andrew Carnegie Research Scholarship.

"Ionic Sizes in Relation to the Conductivity of Electrolytes."

By W. R. Bousfield, M.A., K.C., M.P. Communicated by Professor Larmor, Sec. R.S. Received February 10,—Read March 9, 1905.

(Abstract.)

The law of mass action, which gives us Ostwald's law for weak electrolytes, has not hitherto been harmonized with the empirical data for strong electrolytes. But it may be reconciled with the conductivity data for strong electrolytes as well as weak, on the hypothesis that the ions of an electrolyte consist of molecular aggregates in combination with water, and on this hypothesis gives Van't Hoff's Law.

If Stokes's results as to the motion of a sphere in a viscous fluid be applied to the motion of the ions of a binary electrolyte, it is again necessary, in order to reconcile theory with empirical facts, to make the same assumption, and to suppose that the ions are molecular aggregates largely composed of water molecules, the size of an ion depending upon the amount of water in combination with it, and being a function of the temperature and concentration.

Upon this hypothesis the form of the function may be represented, within a temperature range of 0° to 36° C., and a concentration range (in the case of KCl) from twice decinormal to infinity as

$$r_\infty/r = (1 + \mathrm{AT} + \mathrm{BT}^2)\,(1 + \mathrm{C}h^{-\frac{1}{3}})$$

where h is the "hydration," *i.e.*, the ratio of the molecules of water present to the molecules of the solvent, A and B are the radial temperature coefficients, C the radial concentration coefficient, and T is temperature $- 18°$.

A correction for the coefficient of ionization is thus attained, which gives the true coefficient of ionization in the case of KCl as

$$\alpha = \frac{\Lambda}{\Lambda_\infty} \cdot \frac{1}{f} \cdot \frac{1}{1 + 3{\cdot}33h^{-\frac{1}{3}}},$$

where f is the fluidity of the solution.

With this coefficient of ionization Van't Hoff's law, modified by substituting the "hydration" of the solute for its concentration, gives an accurate agreement with experimental results to within an error of 1 part in 2000 down to twice decinormal solutions—a greater accuracy than has been attained by the best empirical formula hitherto proposed.

The water entering into combination with the ion is probably abstracted from the solvent largely as "trihydrol" or "hydrol," according to the temperature of the solution, and enters into combination with the ion as "dihydrol," thus causing contraction.

In the two cases hitherto investigated it is found that the ionic volumes calculated from the conductivities on the above hypothesis are in agreement with the "solution volumes" calculated from the densities. This is a striking confirmation of the hypothesis and of the soundness of the method adopted.

The expression $(1 + Ch^{-1})^{-3}$, which is deduced from the conductivities as being proportional to the ionic volume changes of KCl, is applied to a consideration of the density law of KCl.

Hence, one arrives at a rational density law for KCl, which represents the experimental values of the density from 1 to 6 per cent. accurately to five places of decimals.

A remarkable difference is manifested in the relation of ionic volume to solution volume as between concentration changes and temperature changes.

For isothermal concentration changes the ionic volume decreases as the solution volume increases, that is to say, with increasing water combination there is increasing contraction, a result which was to be anticipated. But in the case of temperature changes at constant concentration, there is *increasing* water combination with *diminishing* contraction—a quite unexpected result. This result is completely explained by reference to the variation in the proportions of trihydrol and dihydrol in the constitution of water with varying temperature. Assuming that the attack of the ions upon the trihydrol and dihydrol is in proportion to their concentrations at the temperatures considered, the volume changes as determined from the conductivities are shown to be in accord with the volume changes as determined by the densities.

A new variety of viscosity apparatus is described, and a series of measurements of the viscosities and densities of KCl from 0 to 21 per cent. are given.

"The Origin and Growth of Ripple-Mark." By Mrs. HERTHA AYRTON. Communicated by Professor W. E. AYRTON, F.R.S.

Received April 21; received in revised form May 26,—Read June 16, 1904.

(Abstract.)

The object of the investigation was to determine how ripple-mark started in perfectly smooth sand, apart from accidental variations of surface friction; how the ripples grew; how the amplitude and depth of the water affected them; and whether there was any connection between ripple-mark and kindred phenomena, such as the dust figures in a Kundt's tube.

In the course of the investigation the causes, form, and mode of action of "ripple vortices" in the water were determined, and the fact that no vortices of this kind can form in a current flowing steadily in one direction *over* an obstacle was demonstrated, both theoretically and practically. Also many minor details came to light, such as the fact that each ripple is continually travelling, as a whole, and why it does so.

As regards the starting of ripple-mark, it was found that a single ridge forms, on perfectly smooth sand, wherever the water happens to have the same place of maximum longitudinal velocity during several oscillations. That as soon as this ridge is high enough (less than a millimetre is sufficient), the water, in flowing over it, forms a spiral vortex with horizontal axis, which starts a new furrow and ridge in the lee of the first—on one side during one swing and on the other side during the next. That the vortex that forms in the lee of each of these two ripples in turn originates a new ripple there, and that in this way, fresh ripples are begun with each succeeding swing of the water till the whole sand is ripple-marked.

It was shown that the "ripple vortices" only came into existence during the time when the water was rising above the mean level, and the causes and manner of formation of the vortices were given.

It was found that when the place of maximum horizontal velocity was constant, not merely for several oscillations, but for a considerable time, as at the loop, for horizontal motion, of a stationary wave, the ridge mentioned above grew into a ripple-marked heap which was highest at the loop and lowest at the nodes. By oscillating water in the simplest possible way, *i.e.*, so that it alternately rose and fell at one end of the trough while it alternately fell and rose at the other, a stationary wave having its length twice the length of the trough was obtained, and in this case a ripple-marked mound arose of which the apex was at the middle of the trough—one loop of the wave—and

the lowest parts were near the ends—the two nodes. When the stationary wave was of the same length as the trough two mounds arose, one near each end, and so on.

It is suggested that the tidal ridges in estuaries and the chains of sand banks under the sea are formed in this way, by stationary or nearly stationary water waves, and that the sand dunes of the seashore and of the desert, and the clouds in a "mackerel sky" may be similarly the products of stationary air waves.

"The *Rôle* of Diffusion in the Catalysis of Hydrogen Peroxide by Colloidal Platinum." By GEORGE SENTER, Ph.D., B.Sc. (Lond.). Lecturer on Chemistry at St. Mary's Hospital Medical School. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S. Received March 7,—Read March 30, 1905.

According to a theory of reaction-velocities in heterogeneous systems recently put forward by Nernst,[*] the observed velocities are those with which diffusion and convection renew the reacting material at the boundary of the two phases, the actual chemical change at the boundary being very rapid in comparison. Nernst is of opinion that the same considerations apply to the catalytic decomposition of hydrogen peroxide by colloidal platinum and similar substances, but has not gone fully into the discussion of this particular class of heterogeneous reactions.

In a recent paper on the effect of poisons on the catalysis of hydrogen peroxide by hæmase,[†] I have discussed the probable mechanism of catalysis by colloidal particles, and have arrived at the conclusion that the experimental results obtained by Bredig and his pupils and by myself are best accounted for on Nernst's hypothesis.

In an important paper on this subject, Sand,[‡] starting from certain assumptions regarding the size and nature of the particles in a colloidal platinum solution, has calculated the minimum value of the velocity-constant (which we may call K_D) to be expected on Nernst's hypothesis, and finds that it is at least 16 times as great as the velocity-constant obtained experimentally by Bredig.[§] Hence, he concludes that Nernst's hypothesis does not apply to this particular reaction; the observed velocity is really that of a chemical action.

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[*] 'Zeitschrift für physikal. Chemie,' vol. 47, p. 52, 1904.

[†] 'Roy. Soc. Proc.,' vol. 74, p. 201, 1904.

[‡] 'Roy. Soc. Proc.,' vol. 74, p. 356 (1905).

[§] Bredig and Müller von Berneck, 'Zeit. für physikal. Chemie,' vol. 31, p. 258, 1899; Bredig and K. Ikeda, 'Zeit. für physikal. Chemie,' vol. 37, p. 1, 1901.

In another part of his paper Sand discusses the observation of Bredig that the reaction-velocity increases more rapidly than the concentration of the catalysor, and concludes that this can only be accounted for by increased convection owing to the brisker evolution of oxygen when large amounts of catalysor are present.

In the present paper it is shown that when K_D, which is a measure of the maximum rate at which hydrogen peroxide can be supplied to the particles by diffusion, is great in comparison with the observed velocity-constant K, the hydrogen peroxide concentration at the surface of the particles will be maintained by diffusion at a value which does not differ appreciably from the average concentration in the solution, so that increased convection will have practically no effect on the observed reaction-velocity. From this it follows that if, as Sand maintains, increased convection does modify the reaction-velocity considerably, K_D cannot be large in comparison with K, since convection can only modify the value of the former constant.

The question here considered is somewhat analogous to that of a slow chemical action succeeded by a rapid one. Under such circumstances it is the velocity of the slow action which is measured, and it is clear that an increase in the rate of the rapid reaction will have no effect on the observed velocity. It is not *a priori* evident that the same considerations apply to a slow chemical action, accompanied by rapid diffusion, since the constants of the two changes are not directly comparable, though both have reference to the rate of transference of hydrogen peroxide.

If K_D *(as defined above) be* n *times as great as the velocity-constant* K_0 *of the chemical action at the surface of the colloidal particles, the concentration at the boundary will be maintained by diffusion at a value not less than* $(n-1)/n$*th of the average concentration in the solution.*

Let K be the observed velocity-constant and D, as defined below, have a value which does not differ appreciably from the average concentration C of hydrogen peroxide in the solution, then we have, for the rate of fall of concentration in the main bulk of liquid,

$$-dC/dt = KD \quad \text{.........................} \quad (1).$$

Further, let K_0 be the velocity-constant of the chemical action, and C_r the concentration of peroxide close to the surface of any particle, then, if we assume that the reaction velocity is proportional to C_r, we find for the rate of fall of concentration at the boundary due to chemical action (which is of course equal to the observed rate of fall in the main bulk of liquid, since hydrogen peroxide is only removed at the boundary),

$$-dC/dt = K_0C_r \quad \text{.........................} \quad (2).$$

If this loss is just compensated by diffusion inwards towards the particles, we find, from Sand's Equation (19), p. 367, that the amount removed by each particle in the time dt is

$$Fdt = 4\pi kr\gamma(D - C_r)\,dt \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3),$$

where k is the diffusion coefficient of hydrogen peroxide, r is the radius of the particle, and $\gamma = R/R - r$, where R is at such a distance from the particle that the concentration there is D, which does not differ appreciably from the average concentration in the solution.* The amount removed from unit volume containing N particles (where $4/3\pi r^3 N = v$) is N times as great, or

$$= \frac{4\pi k(D - C_r)\gamma v \times 3}{4\pi r^2} = \frac{12kv\gamma(D - C_r)}{L^2} \quad \ldots\ldots\ldots \quad (4),$$

where $L = 2r$ = the diameter of a particle.

Hence
$$K = \frac{12kv\gamma}{L^2}\left(1 - \frac{C_r}{D}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5).$$

Further, since $KD = K_0Cr$, we have

$$K_0 = \frac{12kv\gamma}{L^2}\left(\frac{D - C_r}{C_r}\right) \ldots\ldots\ldots\ldots\ldots\ldots \quad (6).$$

If K_0 is infinite (Nernst's hypothesis) $C_r = 0$, and from Equation (5) we obtain for K, which in this case is K_D, the value

$$K_D = 12kv\gamma/L^2 \ldots\ldots\ldots\ldots\ldots\ldots \quad (7),$$

which Sand shows is at least 16 times as large as the velocity-constant determined by Bredig. Hence, *if Sand's value for K_D be accepted*, we must conclude that C_r is not zero, and that experiment therefore does not justify Nernst's hypothesis.

From Equations (5) and (7) we can readily find the relation between C_r and D. If we deal with the case where K_D is 16 times as large as the observed velocity-constant K, it is obvious that

$$1 - \frac{C_r}{D} = \tfrac{1}{16}, \text{ or } C_r = \tfrac{15}{16}D.$$

In general, if K_D is n times as large as K, we have

$$C_r = \frac{n-1}{n}D \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8).$$

The way in which the observed velocity of a heterogeneous chemical reaction depends upon the relative values of the "diffusion" constant and the "chemical" velocity constant.—From Equation (8) we find that if K_D is great in comparison with K, the concentration at the surface of the particles, with a minimum of stirring, is practically equal to the average concentration in the solution. Since $K_0C_r = KD$, it follows that in this case the chemical velocity-constant K_0 is scarcely different from the observed velocity-constant K.

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* Sand, *loc. cit.*, p. 362.

Just as in the case of successive inter-dependent chemical actions, there are, therefore, three cases to distinguish :—

(1) If K_0 is great in comparison with K_D (Nernst's hypothesis), the observed reaction-velocity depends only on K_D, it is that with which diffusion and convection bring the reacting material to the boundary.

(2) If K_0 and K_D are comparable in value, the observed velocity will depend on both, and will, consequently, be modified by alterations in either.

(3) If K_0 is small in comparison with K_D, the observed reaction-velocity depends only on K_0, and will, consequently, not be affected by such changes as stirring may produce in the value of K_D.

So far as we have gone, it would seem that the platinum catalysis of hydrogen peroxide is an example of Case (3).

The reaction-velocity increases much more rapidly than the Catalysor concentration.—Bredig* has found that, on doubling the amount of his catalysor, the reaction-velocity is trebled instead of merely being doubled, as one would expect if the catalysor particles act independently of one another, and Sand, apparently with good reason, has suggested that this is due to convection currents set up by the rapid evolution of oxygen bubbles in solutions containing large quantities of catalysor. This view as to the great effect of convection currents cannot, however, be easily reconciled with the conclusion arrived at above, that we are dealing with a "chemical" reaction-velocity. We have seen that, in the case considered, C_r, with a minimum of stirring, is $\frac{15}{16}$ of the average concentration in the solution. The effect of stirring would be to shorten the diffusion-layer, and bring C_r nearer to the average concentration; but it is clear that the greatest possible alteration of the reaction-velocity from this cause will only amount to $\frac{1}{16}$ of its value, which is quite insufficient to account for Bredig's results.

In searching for an explanation of this difficulty, we must first consider what evidence there is for the suggestion that the want of proportionality between K and the catalysor concentration is due to the disturbing effect of convection currents. If this is not the case—if an explanation on chemical grounds can be found for the deviation in question—then we must regard the observed velocity as in all probability a chemical velocity. If, on the other hand, the want of proportionality is due to the effect of convection in modifying the reaction-velocity, it is clear that K_D cannot be great in comparison with K, and we must search for a possible error in the assumptions which have led to this conclusion.

The Part Played by Convection Currents.—As Sand has pointed out, "the fact that K increases more rapidly than the catalysor concentration can only be accounted for by supposing that the process taking place on the surface of a particle influences that of its neighbours by some non-chemical means," and it is difficult to imagine any other way in which this can be effected than by the production of convection currents. Sand suggests that these currents are set up in the liquid by the bubbles of oxygen evolved, but this cannot be regarded as a complete explanation of the observed facts. On this view we would expect K to increase with increasing peroxide concentration (owing to the more rapid evolution of oxygen), but this is not the case. It has been found that K decreases,* though only to a small extent, with increased peroxide concentration. Further consideration shows, however, that this apparent contradiction can be satisfactorily accounted for on the convection hypothesis.

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* Bredig and Müller von Berneck, *loc. cit.*, p. 312.

We must, as a matter of fact, consider three possible ways in which K may be affected by the processes in question:—

(1) The particles themselves are in Brownian motion;† they are continually moving into fresh portions of the solution, and thus tend to keep a constant concentration outside the adherent layer through which diffusion is taking place. Further, owing to their motion, they stir the liquid as a whole, and thus, with increasing concentration, the average thickness of the layers on all the particles would be lessened, so that K would increase more rapidly than the catalysor concentration.

(2) Owing to evolution of bubbles of oxygen in the stronger solutions, and consequent stirring of the liquid, the diffusion path would be shortened, and K, as we have already seen, would increase more rapidly than the platinum concentration.

(3) The formation of bubbles on the surfaces of the particles would interrupt the diffusion-layer and tend to retard the action. This process on one particle would not, however, affect that on another, so that, *as far as this effect alone is concerned*, the reaction-velocity would be proportional to the platinum concentration. In solutions containing the same amount of catalysor and different peroxide concentrations, we would expect this disturbing cause to increase with the peroxide concentration, so that the greater velocity to be expected from increased stirring might be more than neutralised by the cause just mentioned. We have thus a simple explanation of the observed fact that K decreases slightly with increase of H_2O_2. The fact that K increases considerably during the action, which has up to the present not been satisfactorily accounted for,‡ is probably due to a combination of the two convection effects just discussed.

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* Bredig and Ikeda, *loc. cit.*, p. 4.

† Senter, *loc. cit.*, p. 218. Compare Spring, 'Bull. Soc. Chim. Belg.,' vol. 19, p. 219, 1900.

‡ Compare Bredig and Ikeda, *loc. cit.*, p. 5; Engler and Wöhler, 'Zeit. Anorg. Chemie,' vol. 29, p. 18, 1901.

In solutions of hydrogen peroxide so dilute that the oxygen evolved would be insufficient to saturate the solution, we would expect K to be proportional to the catalysor concentration, and independent of the peroxide concentration. This has not been directly determined for platinum, but Sand,[*] by collating results in different parts of Bredig's paper, has shown that in solutions containing very little platinum, K is approximately proportional to the platinum concentration. It is strictly true of the hæmase catalysis;[†] only when the evolved oxygen is more than sufficient to saturate the solution do deviations from the simple logarithmic formula appear.

The fact that *all* the observations in the platinum and hæmase catalysis of hydrogen peroxide are thus satisfactorily accounted for on the hypothesis of convection currents, seems a strong argument in favour of the view that the latter play a considerable part in the action.

Possible errors in the assumptions used in calculating K_D.—If the above views as to the part played by convection currents are accepted, we must investigate the assumptions which have led to the conclusion that the value of K_D is great in comparison with that of K. Sand arrived at this result by substitution of probable minimum values for k and v, and a maximum value for L, the diameter of a particle, in Equation (5), $K_D = 12\,kv\gamma/L^2$.

There would seem to be at least three possible sources of error in the calculation of a numerical value for K_D. (1) The value (10^{-5} cm.^{2} per sec.) assumed for k, the coefficient of diffusion of hydrogen peroxide, may be too large. (2) The average diameter L of the particles may be greater than the maximum value assumed by Sand ($0{\cdot}5\mu$). (3) Only part of the platinum surface may be active towards hydrogen peroxide; the value taken for v may thus be too large.

These three possibilities will now be shortly considered:—

(1) Although the diffusion coefficient of hydrogen peroxide has not been determined, there can be very little doubt, from the values obtained with substances of similar molecular weight, that the value assumed for k is not too large, so that an error from this cause is very unlikely.

(2) *The size of the particles.*—Since, according to Equation (7) K_D varies inversely as the square of the diameter of the particles, the velocity calculated on Nernst's hypothesis would correspond with the velocity actually observed if the average diameter of the particles be *four times* the maximum value ($0{\cdot}5\mu$) assumed by Bredig and Sand. Bredig[‡] mentions that his solutions showed no suspended particles when examined under a microscope capable of detecting objects of the diameter $0{\cdot}2\mu$. Although it ought to be borne in mind that particles

[*] *Loc. cit.*

[†] Senter, 'Zeit. physikal. Chemie,' vol. 44, p. 257, 1903.

[‡] 'Anorganische Fermente,' Leipzig, 1901, p. 21.

in motion may not be so readily detected as stationary particles,[*] yet the uncertainty from this cause would be least in the case of large particles, so that it seems very improbable that particles of the diameter μ could escape detection under the above conditions.

Zsigmondy and Siedentopf[†] have investigated the magnitude of the particles in colloidal solutions of gold prepared by reduction; they find many particles of the diameter $1/100\mu$ and others still smaller. Stöckl and Vanino[‡] have independently arrived at the same result. So far as I am aware, colloidal solutions, prepared by Bredig's method, have not been examined by Zsigmondy and Siedentopf's method, but it does not seem probable that such solutions would differ markedly, as regards the magnitude of the particles, from those prepared by reduction.

It may, therefore, be concluded that the want of agreement between K_D and K cannot be accounted for by too low a value having been taken for the magnitude of the particles.

(3) *The suggested inactivity of part of the platinum surface towards hydrogen peroxide.*—Equation (7) has been derived on the assumption that all the particles are active towards hydrogen peroxide. If only some of the particles are thus active, the total reacting surface, which is proportional to v for equal particles, would be diminished, and thus K_D would attain a value more nearly coresponding to K. (It should also be noted that v and consequently K_D would be diminished by the process discussed under the third heading in the section on convection, p. 570, but this effect would, in any case, be small and would completely disappear for solutions in which oxygen is not evolved in bubbles, so that we cannot account in this way for the difference between K_D and K). Nernst[§] has already suggested the possibility that part of the platinum is inactive, and some positive evidence to this effect is to be found in papers by Bredig and Fortner[||] and by Liebermann.[¶] The first two investigators found that the palladium catalysis of hydrogen peroxide is greatly accelerated by previous treatment of the palladium with hydrogen, and the same is true, though to a much smaller extent, of the platinum catalysis. The latter result has been confirmed by Liebermann. Bredig[**] has also found that platinum which has been poisoned with CO is more active after recovery from the poison than platinum which has not been so treated.

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[*] The limit of visibility under the microscope will probably depend upon the number of the particles present in a given volume, as well as on the nature and magnitude of their motion.

[†] 'Zeit. für Elektrochemie,' vol. 8, p. 686, 1902.

[‡] 'Zeit. für physikal. Chemie,' vol. 30, p. 99, 1899. Compare also Lobry de Bruyn, 'Receuil Travaux Chim. Pays-bas,' vol. 19, p. 251, 1900.

[§] *Loc. cit.*, p. 55.

[||] 'Berichte d. deut. chem. Ges.,' vol. 37, p. 805, 1904.

[¶] 'Berichte d. deut. chem. Ges.,' vol. 37, p. 1519, 1904.

[**] 'Anorg. Fermente,' p. 79.

The cause of this increased activity must be, for the present, largely a matter of speculation. It may possibly be due to the breaking up of aggregates of particles and consequent increase of the reacting surface, but a more probable explanation is that the surfaces are partly freed from some impurity which prevents action on the peroxide. The suggestion may be made that this surface impurity is platinous oxide. It has been shown by Mond, Ramsay and Shields,* and by Wöhler,† that this oxide results when platinum is heated in air, and, having regard to the method of preparation of Bredig's solutions, it is to be expected that the platinum will be partly oxidised. This is supported by the observation of Bredig that a trace of his colloidal platinum is dissolved by sulphuric acid. Engler and Wöhler‡ have shown that platinous oxide acts much less energetically on hydrogen peroxide than platinum itself.

It seems probable that, as many investigators have suggested, an intermediate oxide of platinum is formed in the platinum catalysis of hydrogen peroxide, but most likely a higher oxide, perhaps PtO_2, which can react rapidly with the peroxide. This would correspond with Manchot's§ explanation of the great accelerating effect of ferrous salts on oxidations as compared with ferric salts. He has shown that the action proceeds by intermediate formation of a higher oxide of iron, and that the catalytic effect is much lessened when part of the iron has changed to the ferric condition.

Whether this suggestion applies or not, it is clear from what has been given above that there is reason for supposing that the entire platinum surface is not active under ordinary conditions, and this seems the most probable explanation of the difference between K_D as calculated by Sand, and K the observed velocity-constant.

Summary and Conclusion.

It has been shown that the deviations from the simple logarithmic formula in the catalytic decomposition of hydrogen peroxide by colloidal platinum are probably due to disturbances caused by convection currents. It has further been shown that when the velocity-constant calculated on Nernst's diffusion hypothesis is great compared with the chemical velocity-constant, increased convection can produce no appreciable effect on the observed reaction-velocity.

In the case under consideration, therefore, since increased convection modifies the observed reaction-velocity, there must be some error in the assumptions which lead to the conclusion that the diffusion velocity-constant is great in comparison with the chemical velocity-constant. This error is probably to be found in the assumption that the whole surface of the platinum is, under ordinary conditions, active towards hydrogen peroxide.

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* 'Zeit. physikal. Chemie,' vol. 25, p. 685, 1898.

† 'Zeit. Anorg. Chemie,' vol. 36, p. 3475 (1903).

‡ 'Zeit. Anorg. Chemie,' vol. 29, p. 13, 1901.

§ 'Annalen der Chemie,' vol. 325, p. 93, 1902.

We are not entitled to assume, from the above considerations, that Nernst's hypothesis is true for the platinum catalysis, but only that the diffusion-velocity is not great in comparison with the chemical velocity (Cases 1 and 2, p. 569). Other considerations, however, such as the small value of the temperature coefficient, make it probable that the above hypothesis does apply to this particular action. Further support for this view may, perhaps, be found in the fact that the deviations from the simple logarithmic law in catalysis by platinum have their exact analogy in the hæmase catalysis. On the "chemical" velocity hypothesis it would seem rather remarkable that two catalysors of so different origin should show exactly similar behaviour, but this becomes at once intelligible on Nernst's hypothesis, according to which the chemical action plays quite a secondary part in the reaction-velocities in question.

In conclusion, I wish to acknowledge my obligations to Professor A. W. Porter and Dr. Sand, with whom I have had the advantage of discussing the subject-matter of the present paper.

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